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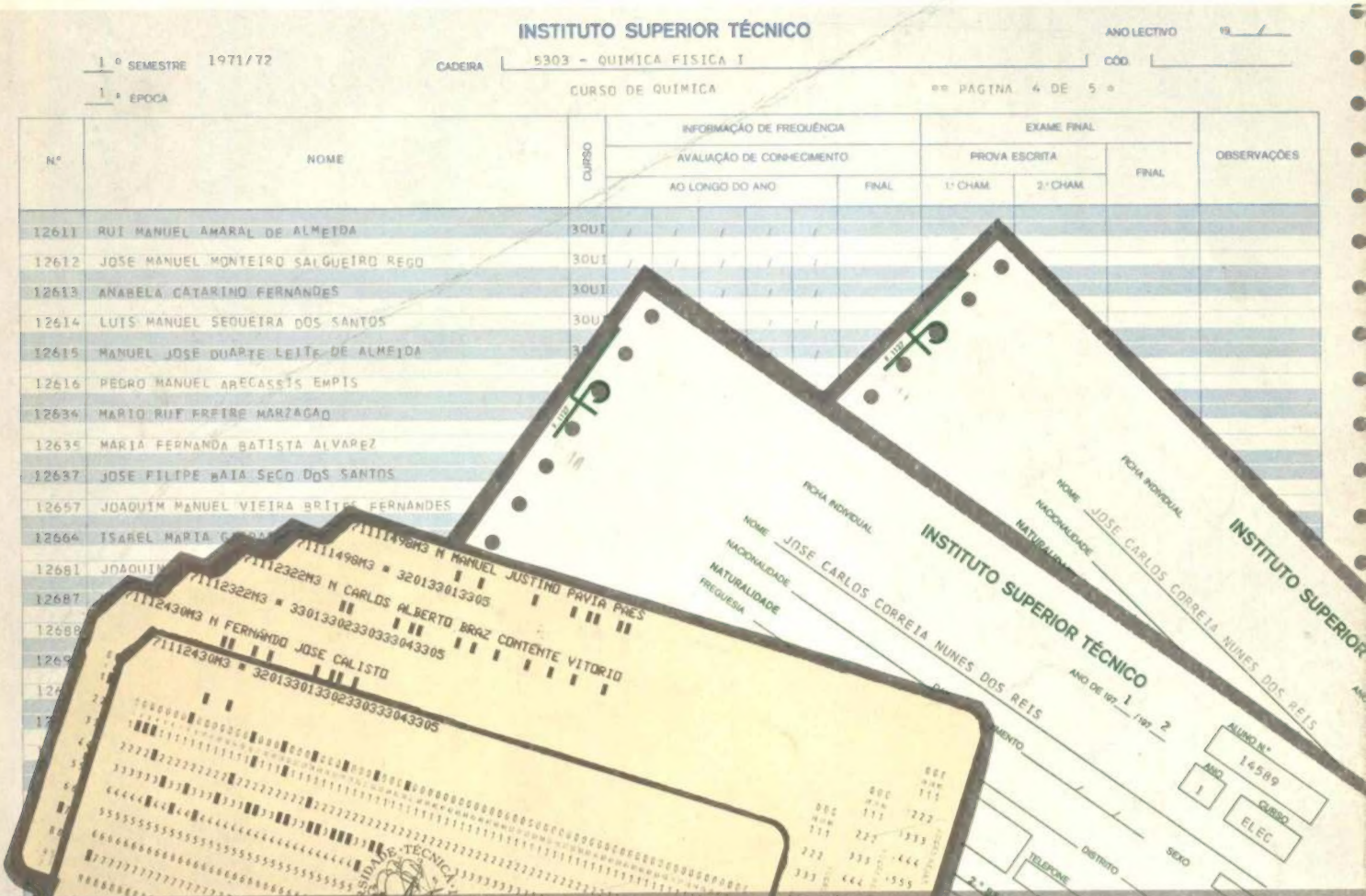

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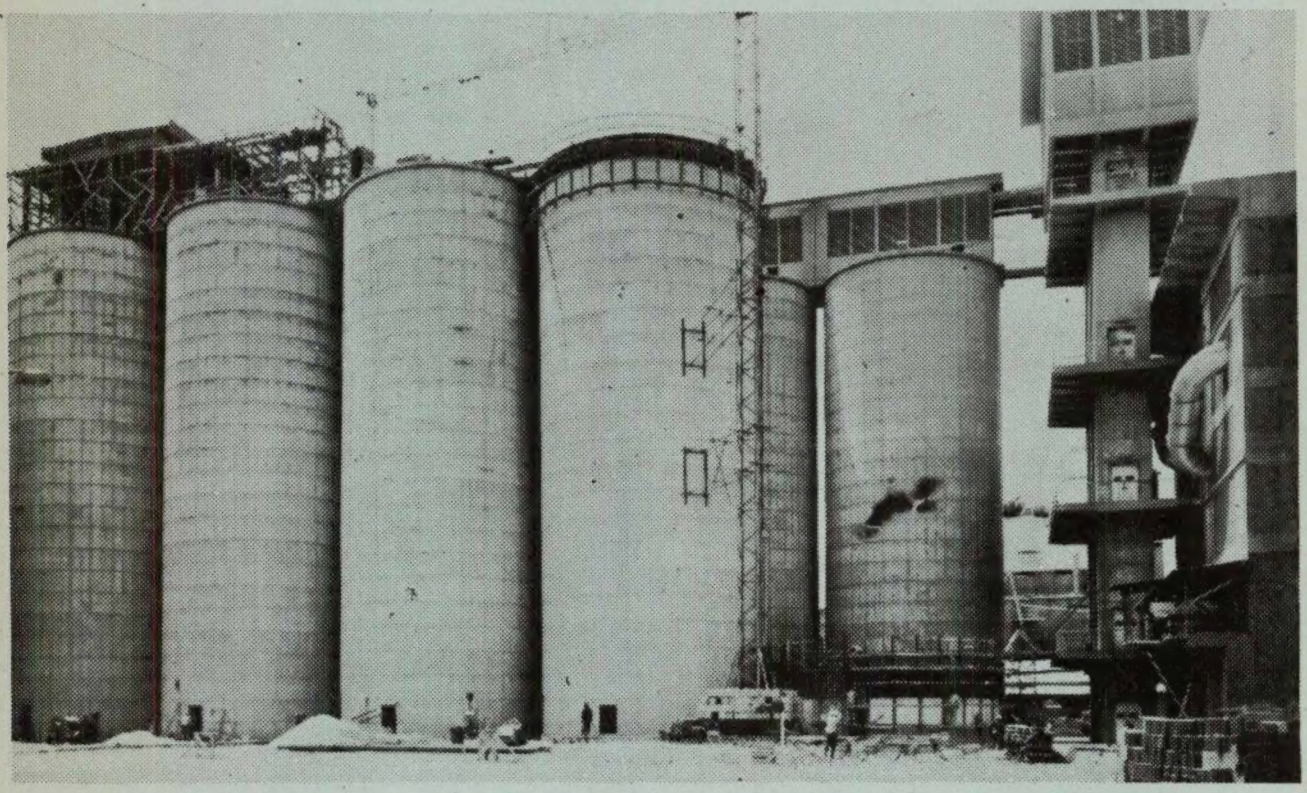

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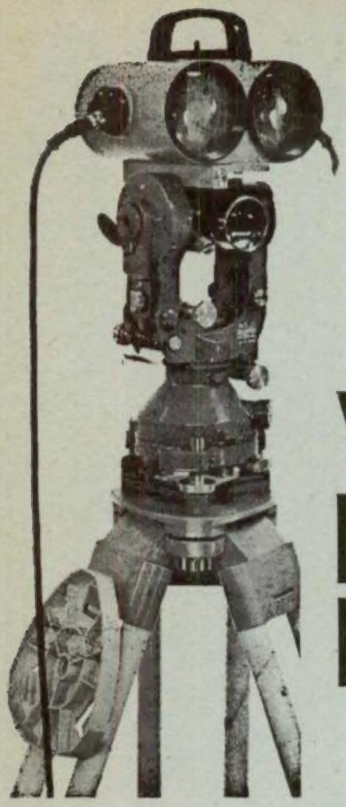

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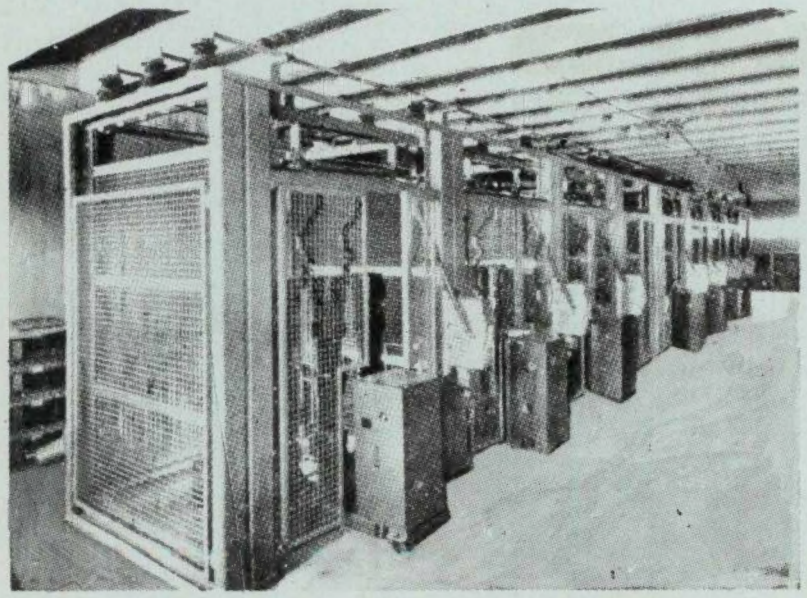

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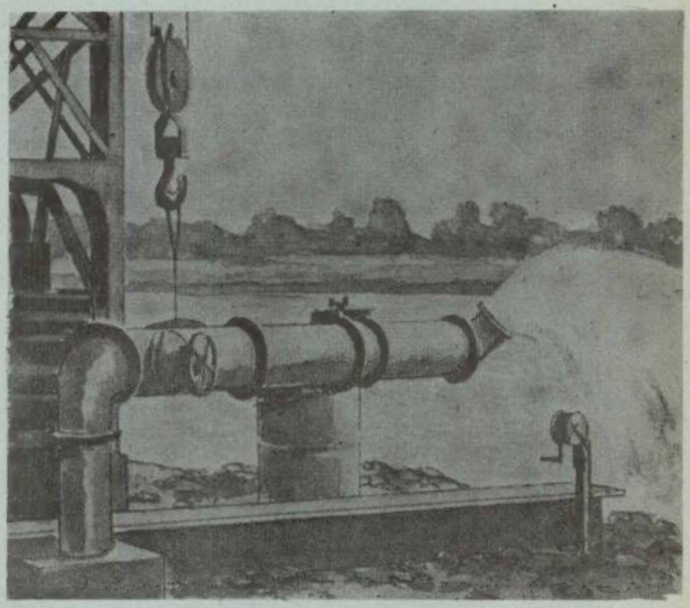

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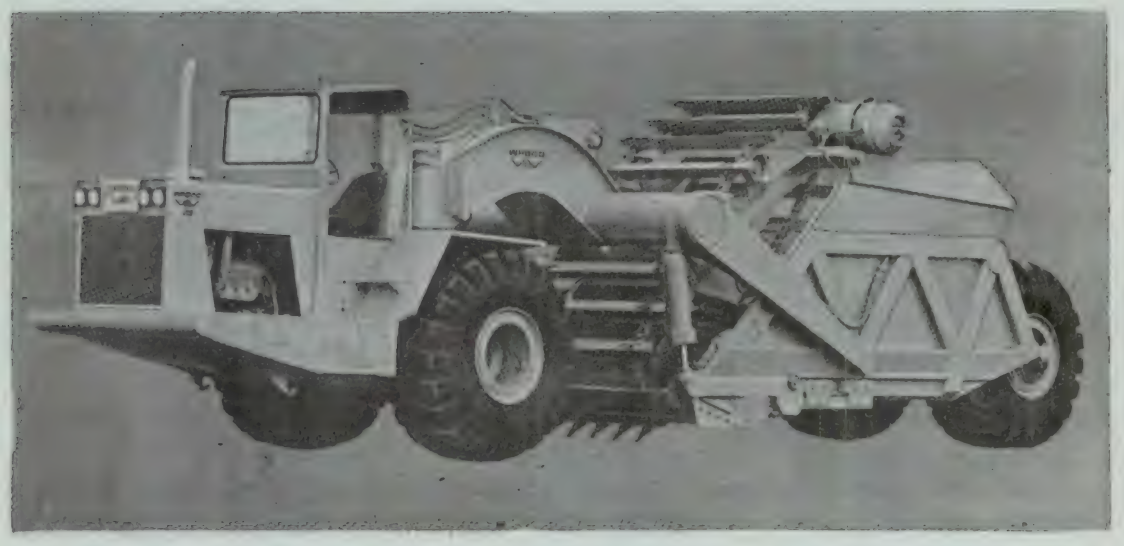

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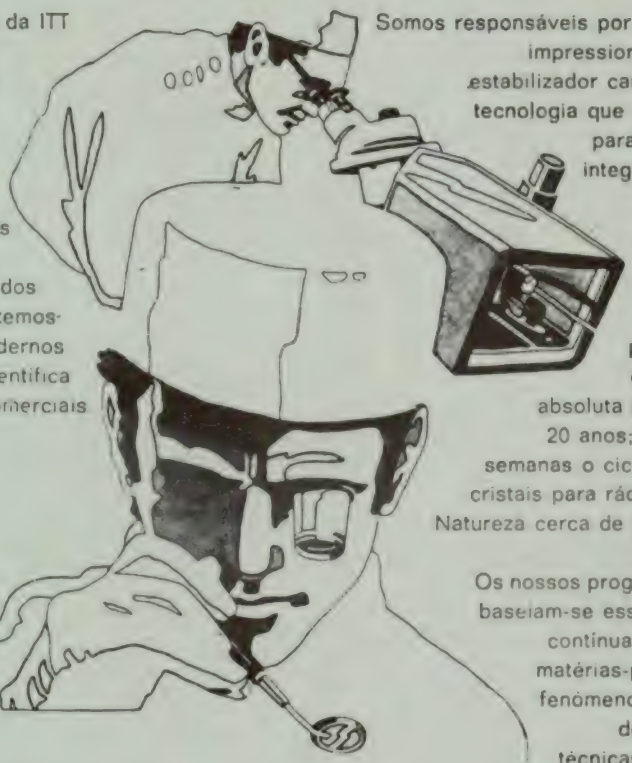

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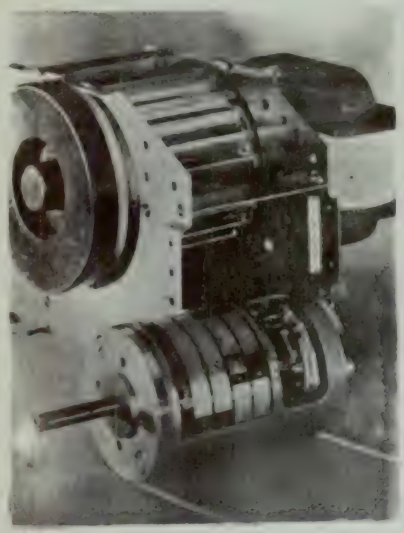

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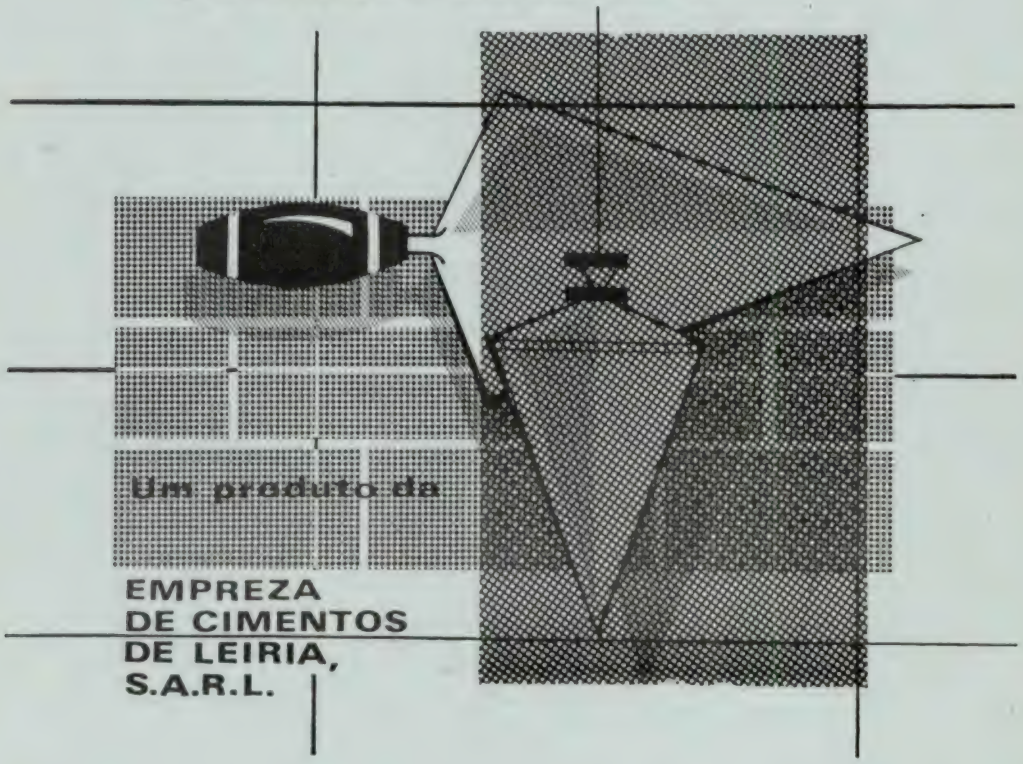

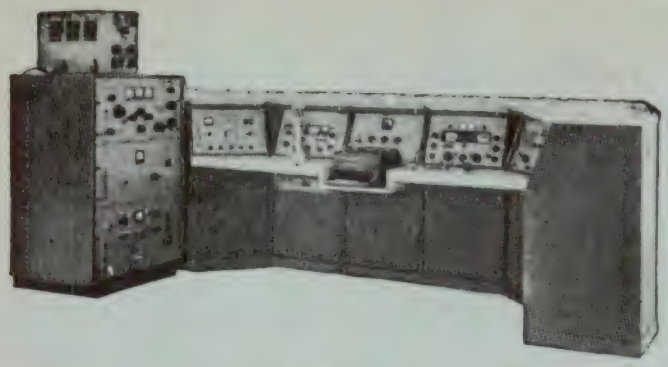

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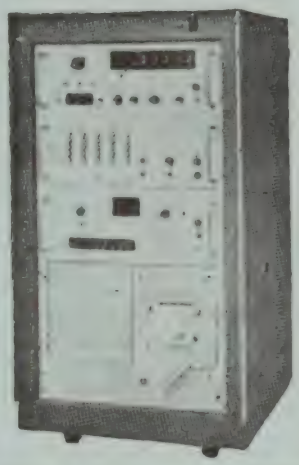

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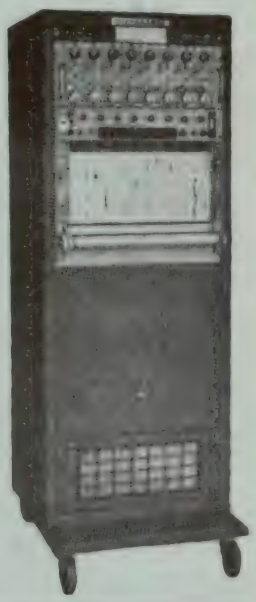

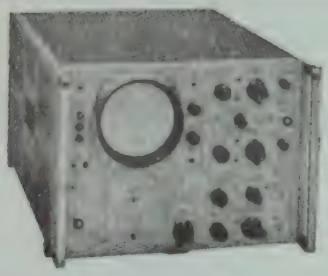

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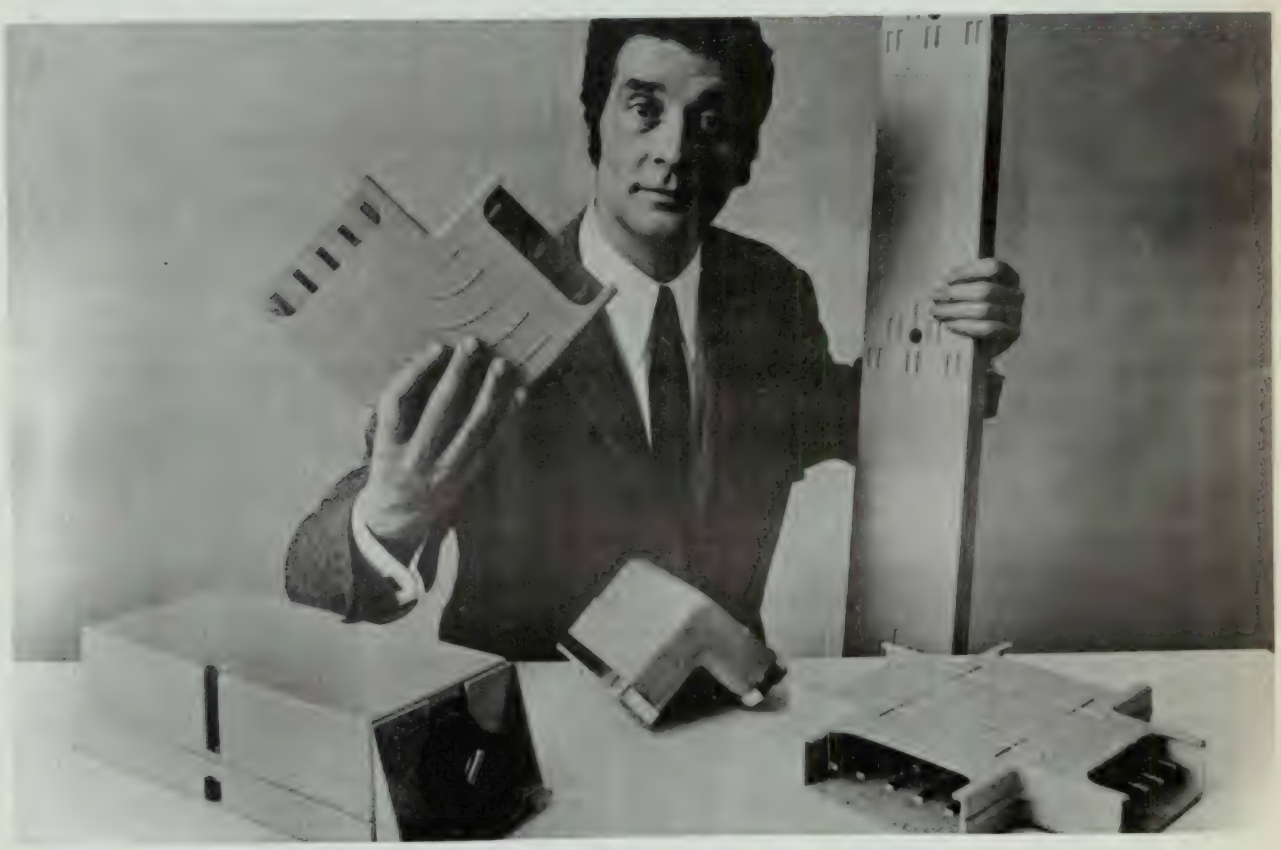

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DISORDER IN CRYSTALS

by L. A. K. STAVELEY
(The Inorganic Chemistry Laboratory, Oxford University)

SYNOPSIS

A general survey of order - disorder phenomena in crystals is presented. Several types of disorder are considered, with special emphasis on disorder of position, disorder of orientation and magnetic disorder. A review of the main experimental techniques used in these studies is given, as well as a general discussion of some theoretical treatments.

RESUMO

Apresenta-se uma revisão do problema da ordem--desordem em cristais, focando-se em especial os casos de desordem de posição, desordem de orientação e desordem magnética. Faz-se uma discussão dos métodos experimentais mais utilizados no estudo destes problemas, bem como dos tratamentos teóricos mais correntes.

A. TYPES OF DISORDER

Any crystal, however perfect, is in a sense always disordered. It can only be regarded as achieving zero entropy at OK, the absolute zero, a temperature which (according to the third law of thermodynamics) can never in fact be reached. However, the non-zero entropy, and hence the disorder, which a crystal inevitably possesses is in general a result of the distribution of its energy among the various possible vibrational and other energy levels available to the particles in the lattice. In this article we shall consider more specific kinds of disorder, namely the following: (1) Disorder of position. (2) Disorder of orientation. (3) Magnetic disorder.

(1) *Disorder of position.* This can arise in more than one way.

(a) Two or more kinds of particle can be randomly arranged on a given set of lattice sites. This situation is encountered, for example, in alloys. [1,2] Thus, the alloys CuZn and FeAl exist in an ordered low temperature form, and a high-temperature disordered form. In each of these two alloys, the lattice sites are the same in both ordered and disordered forms, namely those of a simple body-centred cubic lattice. In the ordered form of, say, FeAl, each Fe atom is surrounded by eight Al atoms, and *vice versa*, whereas in the disordered form the two kinds of atom are mixed up on the available sites, so that an atom of either kind is, on average, surrounded by four Fe atoms and four Al atoms. In certain alloys, only some of the atoms are involved in the disorder. For example, in the alloy Fe_3Al two thirds of the Fe atoms have fixed positions in the lattice in both the ordered and disordered forms, while one-third of the Fe atoms and all of the Al atoms are mixed up on the remaining sites in the disordered high-temperature form.

(b) There are more sites in the lattice than particles available to fill them. A famous case of this is ice, where the number of possible sites for the protons is twice the number of protons. Another example is the solid $Hg(NH_3)_2Cl_2$, which has a cubic unit cell[3]. Here, the Cl^- ions have fixed positions (at cube corners), and the N atoms have fixed positions (at the cube centres). The Hg atoms are situated at the face-centres of the cubes, but there are six times as many of these positions as there are Hg atoms to fill them. The Hg atoms are randomly distributed among these positions, so that the chance of any particular face-centre being occupied is 1/6. An extreme example of positional disorder is encountered in silver iodide, AgI.[4] At about 146°C this undergoes a transition into a high temperature form with a remarkably high electrical conductivity, (comparable with that of a fused salt.) This is because in the high-temperature form, whereas the iodide ions occupy fixed positions in the lat-

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tice, the silver ions move freely between them. One might describe the high-temperature disordered crystal as fluid silver ions moving in a solid formed by the iodide ions.

(c) Although in this article we shall not explicitly consider lattice defects and non-stoichiometric solids, it is worth noting that thermal agitation can create vacant lattice sites in a crystal (so-called Schottky holes or defects), and that these can make it possible for the particles in the lattice to move from one site to another. More information on this will be found in Section F.

(2) *Disorder of orientation.* This arises when a diatomic or polyatomic molecule or ion has more than one distinguishable orientation in the crystal lattice. (The possible orientations must be recognizably different with reference, say, to the crystal axes.) Examples of this are very common and are to be found in simple molecular crystals (e.g. HCl, H_2S, N_2, O_2, CH_4), in more complex organic crystals of which examples will be given later (Sections E and F), and in ionic solids (e. g. certain salts containing ions such as NH_4^+, CN^-, NO_3^-). A simple illustration is provided by ammonium choride. The structure of this, in both ordered and disordered forms, is like that of CsCl. In the tetrahedral NH_4^+ ion, the positive charge is distributed among the hydrogen atoms, and it is natural to expect that each N — H bond will point towards a Cl^- ion. Any one NH_4^+ ion, situated at the centre of a cube of eight Cl^- ions, can so direct its four N — H bonds in just two ways (Fig. 1).

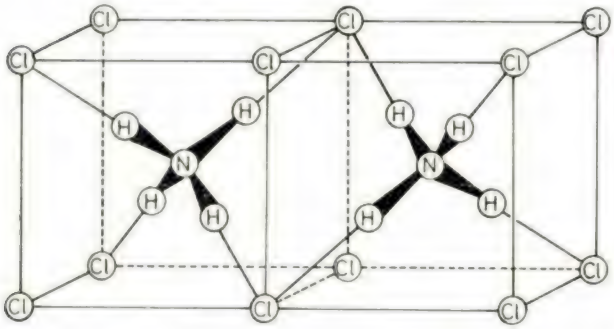
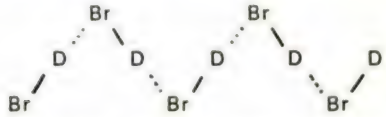


Fig. 1. Showing the two orientations available to an NH_4^+ ion at the centre of a cube of Cl^- ions in NH_4Cl.

In the low-temperature ordered form, all NH_4^+ ions adopt the same orientation, that is they are all parallel. (This is because the electrostatic interaction energy between adjacent NH_4^+ ions is lower in this arrangement). In the high-temperature disordered form, each ion makes use of the two possible orientations available to it, so that at any instant two adjacent tetrahedra may be parallel or they may be antiparallel.

As another example of orientational disorder we may cite the case of deuterium bromide[5], DBr which exists in three forms: I (the high-temperature form), II (the middle form), and III (the low-temperature form). [This, incidentally, illustrates the more or less accepted way of numbering different phases]. In DBr-III, all atoms, both D and Br, occupy definite positions in parallel zig-zag chains, each chain being of the kind



In DBr-II, each DBr molecule has two possible orientations, and can direct its D atom towards one of two neighbouring Br atoms. DBr-I is a face-centred cubic lattice in which any one molecule has twelve nearest neighbours, and it may direct its D atom towards any one of these.

The limit of orientational disorder is free rotation of the molecule or ion. This was at one time thought to be common, and transitions at which free rotation was believed to begin in a lattice were often spoken of (and sometimes still are) as 'rotational transitions'. It now seems fairly certain that free rotation, in the literal sense, is very rare. One of the few cases in which it actually happens is in a crystal of n-H_2, (that is, normal hydrogen consisting of 3/4 ortho-molecules and 1/4 para--molecules), where, near the melting-point at least, the ortho-molecules can undoubtedly rotate freely in the lattice.

(3) *Magnetic disorder.* Ions of transition metals and rare-earth elements which have unpaired electrons behave as elementary magnets, and if a lattice contains such ions these must interact to produce, at sufficiently low temperatures, an ordered spin system. The ordering can be of two basic kinds. Either the spins can line up in the same direction, in which case the magnetic moments reinforce each other to produce a ferromagnetically ordered system, or else the spins order themselves in a self-cancelling way to give an antiferromagnetically ordered structure. A variation of the latter type of ordering is when the crystal contains two sorts of magnetic particle with different moments, as in Fe_3O_4, so that even if the spins of the two kinds of particle adopt an antiparallel alignment they do not completely cancel. A domain of cells therefore has a resultant magnetic moment. Such a solid is termed a ferrimagnetic. The magnetically disordered state in a transition or rare-earth compound is simply, of course, the normal paramagnetic condition, in which the spins are randomly orientated but tend to align themselves in an external magnetic field. The temperature at which they adopt one of the ordered arrangements just described can vary greatly. It may be several hundred degrees Kelvin, or it may be below 1 K. There is one very common molecule where the possibility of magnetic ordering in the crystal arises, namely oxygen.

(4) The above three types of disorder do not exhaust the possibilities. Sometimes the particles in the lattice (certain rare-earth ions are examples) have available to them two or more electronic energy levels, and as the temperature rises the ions gain access to the higher levels with absorption of energy. And some times interesting thermal phenomena are encountered at very low temperatures which have their origin in nuclear

spin and tunneling through energy barriers. Examples of this have been found in methane[6] and in nickel hexammine iodide.[7]

(5) We may end this section with some general observations. One is that the distinction we have made between positional and orientational disorder is sometimes rather arbitrary. For example, the disorder in ice can be thought of as a matter of positional disorder of the hydrogen atoms among the more numerous positions which they can occupy in the lattice (subject to the condition that the unit in the lattice is H_2O and that only one hydrogen atom can lie on the line between any two adjacent oxygen atoms), or alternatively as a question of the orientational disorder of the bent H_2O molecule in the lattice. Anothed point worth making is that a crystal can sometimes simultaneously display more than one kind of disorder. Thus, in lithium iodide monohydrate (LiI, H_2O), which has a perovskite structure (Fig. 2), only the iodide ions and the centres of the water molecules have definite positions.[8] The Li^+ ions are statistically distributed among the face-centres of the unit cube

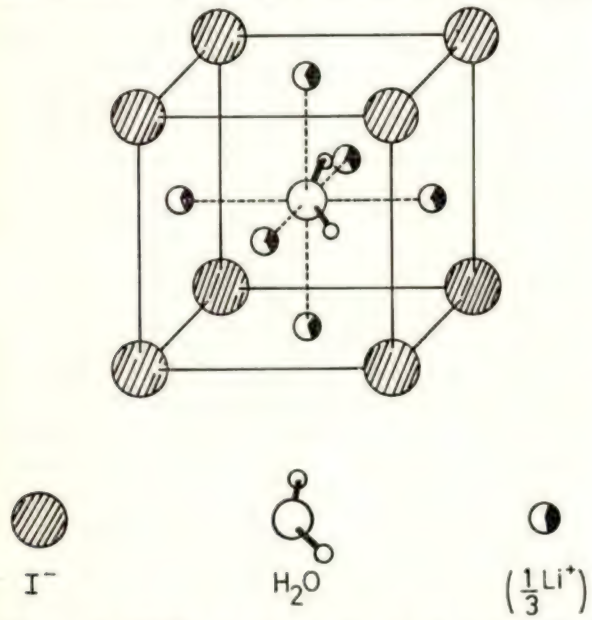


Fig. 2. The structure of LiI,H_2O. The Li^+ ions are situated at the face-centres. The chance that any one face-centre is occupied by an Li^+ ion is 1/3. The H_2O molecules are orientationally disordered.

(and so are positionally disordered), while each water molecule (which is at the centre of the cube, surrounded by eight I^- ions) is orientationally disordered, as there are various ways in which it can direct its two hydrogen atoms towards two of these eight I^- ions.

Finally, a distinction should be made between long - range order and short - range order in a crystal. In saying that at high temperatures the alloy FeAl is completely disordered, we mean that on average any site in the lattice (picked at random) is equally likely to be occupied by an Fe atom as by an Al atom, and that there is no correlation between the nature of the particular atom at any one site and of those at sites some distance from it. (In the perfectly ordered crystal, by contrast, it is sufficient to say this particular site is occupied by an Fe atom to determine which kind of atom occupies every other site in the crystal, however remote). However, the nature of the low-temperature ordered crystal shows that an Fe atom prefers (on energy grounds) to have Al atoms rather than Fe atoms as its nearest neighbours. Hence, by the well-known Boltzmann principle, which requires that in any system of particles there must always be some preference for configurations or arrangements of lower rather than higher potential energy, even in the disordered alloy there will be some tendency, however slight, for an Fe atom to prefer Al atoms as its nearest neighbours. This gives rise to some local, or short-range order. In general in this article we are considering average, or long-range, order.

B. TEMPERATURE AND DISORDER

(1) If a crystal, disordered in one of the ways described above, is cooled down, it generally (though not always) becomes ordered, essentially because the ordered condition is a state of lower energy. It is perhaps better to think of the process in reverse, that is as an ordered crystal being heated up from a low temperature. The change to a disordered crystal can then occur in two ways.

(a) Isothermally, in a so-called first-order phase change. An example is provided by the II $\rightarrow$ I phase change in HCl at 98.4 K. Here the structure changes from a face-centred orthorhombic lattice in which the molecules are orientationally ordered, to a face-centred cubic structure in which they have twelve-fold orientational disorder. At such a transition there is an abrupt change in the enthalpy H, entropy S, and volume V, and in the first differential coefficient, $(\partial G/\partial T)_p$, of the Gibbs energy — hence the term 'first-order'.

(b) Gradually, that is over a range of temperature. Such a transition is revealed by a so-called 'anomaly' in the heat capacity C_p. Over a range of temperature (the extent of which can vary greatly) C_p is higher than it would 'normally' be. The 'extra' heat capacity, plotted against temperature, looks something like the Greek letter λ, and transitions of this kind are frequently described as λ-type transitions. The order-disorder transition in ammonium choride which we have already mentioned is of this kind. Two λ-type transitions are shown by potassium cyanide[9], KCN (Fig. 3). Such gradual transitions are very common, occurring in solids of almost all chemical types (and the one known transition in a purely liquid system, that between the two forms of liquid helium, is of this kind). λ-type transitions may, or may not, involve a change in the basic crystal structure. Thus, in ammonium chloride, this is simple cubic both above and below the transition. In KCN the two lower forms are orthorhombic, but the high-temperature form is face-centred cubic.

The essence of a gradual transition is that it is co-operative in nature. This requires that the change

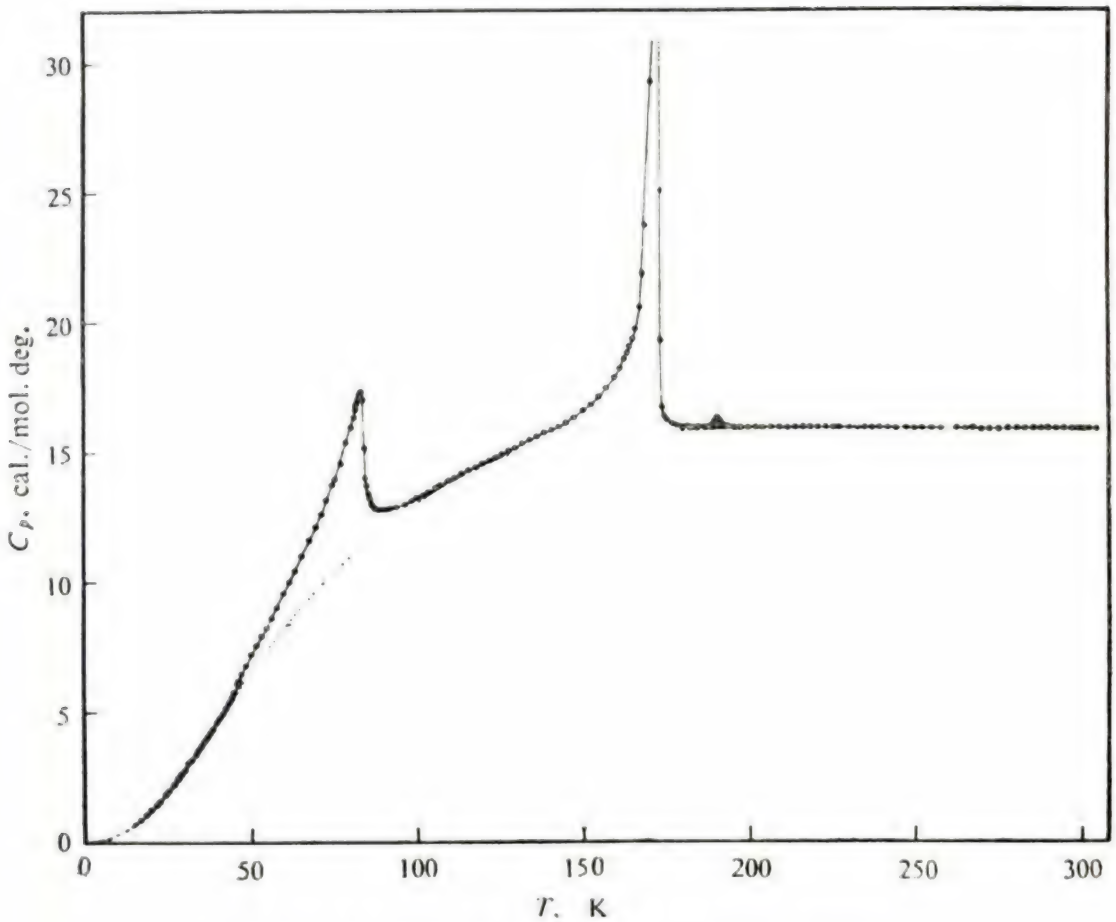


Fig. 3. Plot of the molar heat capacity (C_p) of KCN against temperature.

order → disorder becomes energetically easier, the more disorder there is in the system. The change may be thought of as analogous to a chemical reaction in which the 'reactants' are the ordered crystal and the 'products' the disordered crystal, and in which the change from 'reactants' to 'products' is endothermic — but with this essential difference from a conventional chemical reaction, that in the change from order to disorder the heat of the 'reaction' decreases as the 'reaction' proceeds, becoming zero when it has gone over completely to the 'products' side.

Order-disorder transitions in crystals cannot really be divided sharply into two kinds, namely either first-order (wholly isothermal), or completely gradual. Probably many transitions begin gradually but reach completion isothermally. Whether this is so in any particular case is best examined experimentally by using a property which can be accurately measured at a series of fixed temperatures, for example volume or dielectric constant, rather than the heat capacity (the measurement of which means heating the sample over a range of temperature, even though this may be small). Thus, a careful dilatometric study of the transition in NH_4Cl (often quoted as a typical λ-type transition) showed that the transition begins gradually but is completed isothermally.[10] (By contrast, the corresponding transition in ND_4Cl is completely gradual[11] — an example of the sensitivity of the details of transitions of this kind to the nature of the particles in the crystal.)

(2) Sometimes a disordered crystal remains disordered when cooled down to the lowest possible temperature. Examples of familiar substances which behave in this way are H_2O, CO, NO, N_2O and Na_2SO_4, $10H_2O$. Such a crystal then appears to disobey the third taw of thermodynamics, in that it retains entropy at OK. We shall call this entropy S_{res}, (res = residual). S_{res} can be determined by comparing the value of S_{cal}, the apparent calorimetric entropy of the substance in some defined state (e.g. at 25°C and 1 atmosphere pressure) with the 'true' value of the entropy in this state. This latter quantity will be given for a molecular substance like CO by S_{spec}, the entropy calculated from spectroscopic data using the standard methods of statistical mechanics, or alternatively for a substance which is solid or liquid in the defined state by S_{eq}, the value obtained from some suitable equilibrium study. S_{cal} will be given by $\int_0^T C_p/T\,dT + \Sigma\Delta H/T$ where C_p is the experimentally determined heat capacity and $\Sigma\Delta H/T$ takes account of the entropy increases at phase changes or transitions.

Examples of the determination of S_{eq} will be given later. S_{res} is, of course, the difference between S_{spec} (or S_{eq}) and S_{cal}.

If a crystal remains disordered down to OK, it is generally not because the ordered and disordered configurations have equal energies. The ordered state will still be expected to have the lower energy, but the energy difference is now relatively small, so that it only becomes significant at relatively low temperatures — at temperatures so low, in fact, that by the time they are reached the particles in the lattice find it impossible to undergo the necessary rearrangement to give the ordered crystal in a reasonable period of time. So a crystal like solid N O, which is still disordered at OK, is not really in a true equilibrium state. The disorder has been frozen in, as it were.

C. EXPERIMENTAL METHODS

A wide variety of experimental methods is now used in investigating disorder in crystals. The most important of these are briefly listed below, with examples of the sort of information they provide.

(1) *Thermodynamic studies.* These are inevitable at some stage of the investigation, and indeed most order--disorder transitions have been discovered by heat capacity investigations, which have either revealed a first-order phase change or a gradual λ-type transition. If the transition is gradual, the heat capacity determinations can lead to information on how the extra entropy is acquired. Thus, for magnetic transitions in particular, sometimes only a relatively small fraction of the total entropy taken in during the transition has been gained at the temperature at which the maximum in the heat capacity is reached, implying that considerable order still persists above this temperature (Section H). Moreover, as we shall see, entropies of order-disorder transitions are sometimes (though by no means always) capable of a simple and informative statistical interpretation. And, as already mentioned, the study of crystals which remain disordered down to OK requires the experimental thermodynamic work necessary to give S_{cal}, and (if appropriate) S_{eq}.

In experimental thermodynamics, pressure is much less often varied than temperature, and undoubtedly a good deal of interesting work remains to be done on the effects of high pressure on disordered crystals. One system which has been very thoroughly investigated under pressure is ice, and we shall later refer briefly to some of the high-pressure forms of this solid.

(2) *Diffraction methods.* Since we are dealing with solids, X-ray diffraction methods are of great importance. They have their limitations, however. They do not, for example, in general distinguish between the genuine free rotation of an ion or molecule (though on other evidence this is almost certainly a very rare occurrence, as we have said) and its orientational disorder between a limited, definite number of directions. In seeking a thorough understanding of particular cases of disorder, it is obviously sensible and desirable to study crystals in which the ions or molecules are relatively small. Solids composed of small molecules are often gaseous at ordinary temperatures (e.g. N_2, O_2, F_2), so that the experimental diffraction work on such crystals must be carried out at a low temperature. An example of what can be achieved is shown in Fig. 4, which represents the crystal structure

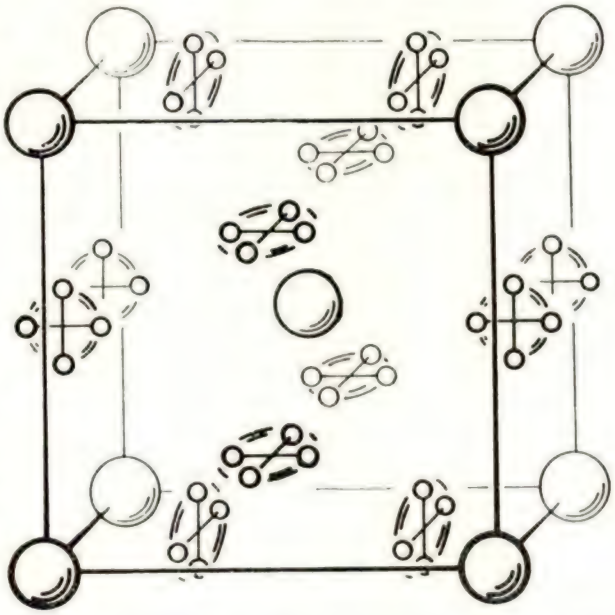


Fig. 4. The structure of the high-temperature form of fluorine, (F_2 – I, = β – F_2). The balls represent F_2 molecules which have orientational disorder in three dimensions. The remaining F_2 molecules are orientationally disordered in two dimensions, (i.e. in a plane).

of the high-temperature disordered form of fluorine, as determined by Lipscomb and co-workers[12]. This is a particularly interesting structure, as the molecules fall into two groups, those of one group being orientationally disordered in three dimensions (spherically disordered), those of the other group in two dimensions only (cylindrically disordered). The limitations of X-ray diffraction in locating light atoms in a solid, particularly hydrogen atoms, are of course well-known, and in this respect electron diffraction can be a somewhat superior technique. Thus, the disordered structure of ice has been confirmed by an electron diffraction study.[13] But still more valuable for locating hydrogen atoms is the technique of neutron diffraction, usually performed on the deuterated compound. Elegant work has been carried out, for example, on hydrogen and deuterium halides by Sandor and his colleagues, in some case with a degree of refinement which actually makes it possible to eliminate the possibility of free rotation in favour of reorientation between a definite number of orientations. Thus, Sandor and Farrow[14] have shown that in the high-temperature face--centred cubic form of DCl, the molecules are not freely

rotating but are distributed among twelve possible orientations (each molecule having twelve nearest neighbours), (Fig. 5). Furthermore, since the neutron has a magnetic moment and interacts with an unpaired electron, neutron diffraction is a powerful tool in investigating magnetic order in crystals, which has been much used in studying compounds of transition metal and rare-earth metals. With solid oxygen, which exists in three forms, there is the possibility of both magnetic

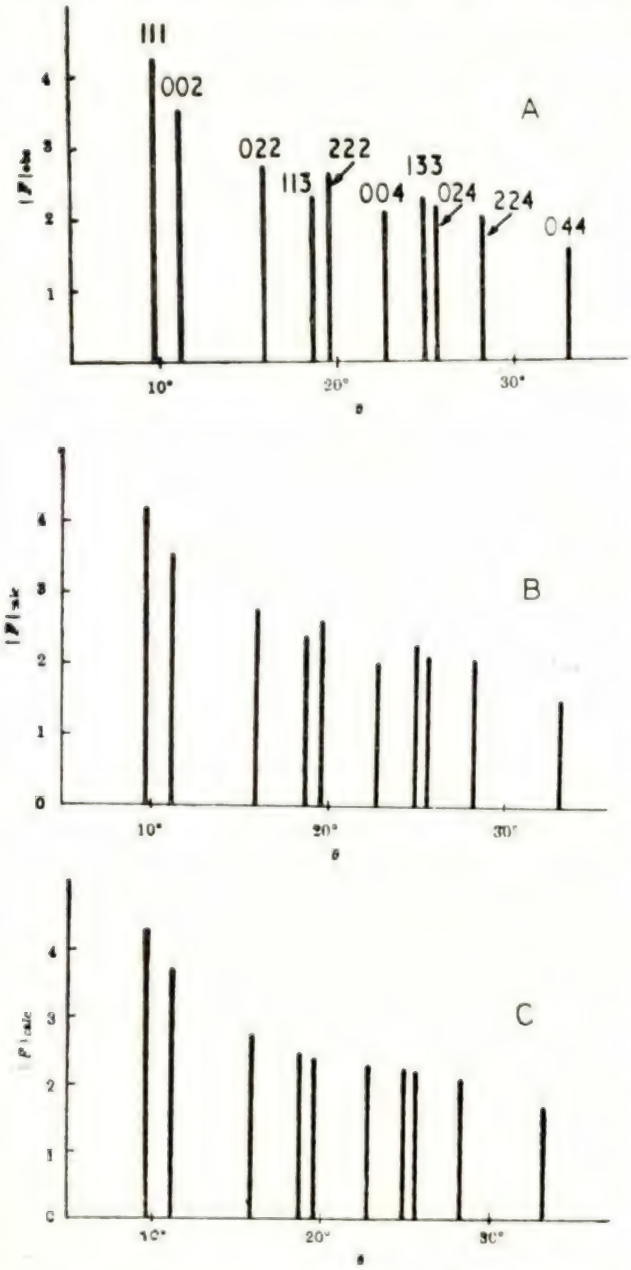


Fig. 5. Neutron diffraction study of DCl — I, the cubic high-temperature form. |F| is the intensity of the diffraction maxima, and θ is the diffraction angle. A shows the experimental results, B is the calculated pattern for a disordered model in which each DCl molecule has twelve possible orientations, and C is the calculated pattern for randomly orientated (freely rotating) molecules. It will be seen that the agreement with A is better for B than for C.

and orientational disorder. A neutron diffraction study of the lowest temperature form III (= α) and of the middle form II (= β) made it clear that III, but not II, is magnetically ordered,[15] (Fig. 6). It will be seen from Fig. 6 that the two low-angle peaks shown by phase III are not given by II, and their appearance for III must be due to the magnetic ordering of the oxygen molecules in this phase. It will be noticed, however, that for phase II the experimental curve for the intensity of the diffracted neutron beam shows a slight bump in place of these two peaks, implying that there is still a tendency towards local magnetic order in this phase, though, of course, no long-range order.

(3) *NMR (Nuclear Magnetic Resonance).* This technique has been especially valuable in giving information about the kinetics of the molecular movements associated with disordering processes, that is about the rate at which molecules or ions can change their orientations or move from one lattice site to another, and about the activation energies for these processes.[16] Use has been made of the effect of temperature on line-widths, second moments, and spin-lattice (T_1) and spin-spin (T_2) relaxation times. As just one example of the sort of behaviour encountered on passing from an ordered to a disordered crystal, we reproduce in Fig.7 the temperature dependence of the linewidth of pentaerythritol, $C(CH_2OH)_4$.[17] This substance undergoes a first-order transition to a disordered phase which exemplifies a type of solid called a plastic crystal (Section F). The linewidth starts to decrease below the transition-temperature due to the gain by the molecules of orientational freedom. The activation energy for the reorientation process is 25.2 kcal mol^{-1}. In the plastic phase the linewidth decreases still further to relatively very small values. This further decrease is ascribed to the ability of the molecules to move rapidly from one lattice site to another, with an activation energy estimated to be 24.3 kcal mol^{-1}.

(4) *Dielectric constant studies.* For molecular crystals with polar molecules (e.g. HCl, H_2S, H_2Se), the acquisition of orientational freedom can often be revealed by studying the temperature-dependence of the dielectric constant (d.e.c.)[18]. For the ordinary substance with polar molecules which exists in just one form (e. g. nitromethane, CH_3NO_2), the d.e.c. of the crystal is relatively small, since the molecules in the lattice are unable to change their orientation when placed in an external electrical field. The d. e. c. of such a substance rises abruptly at the melting-point. For HCl, on the other hand, the d.e.c. increases sharply at the first-order transition from the orientationally ordered form II to the orientationally disordered form I. When I melts, the d. e. c. actually drops due to the expansion on melting.

Valuable information on the kinetics of the reorientation of polar molecules in crystals can be obtained from studies of the phenomenon of dielectric dispersion (essentially the change of d. e. c. with frequency). Examples of this will be found in a paper by Cole and Havriliak.[19]

(5) *Infra-red Raman spectra.* The infra-red spectrum of a crystal can be studied both in the near infra-

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TURBINAS HIDRÁULICAS	*Fabrico segundo licença de A. C. M. de Vevey, S. A.*
TURBINAS A VAPOR	*Fabrico segundo licença de Brown Boveri, Cie.*
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CONSTRUÇÕES METALOMECANICAS **MAGUE** S.A.R.L

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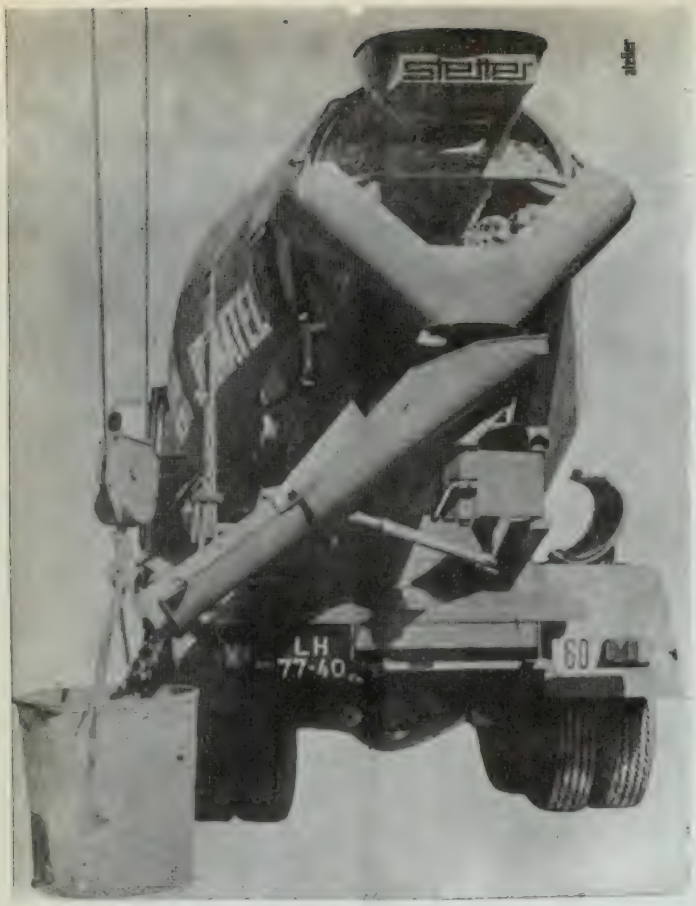
TECNICA XIII



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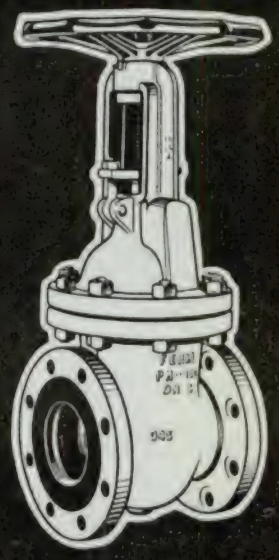

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(incluindo Cl, NH_3 e SO_2).
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vazado, aço inoxidável
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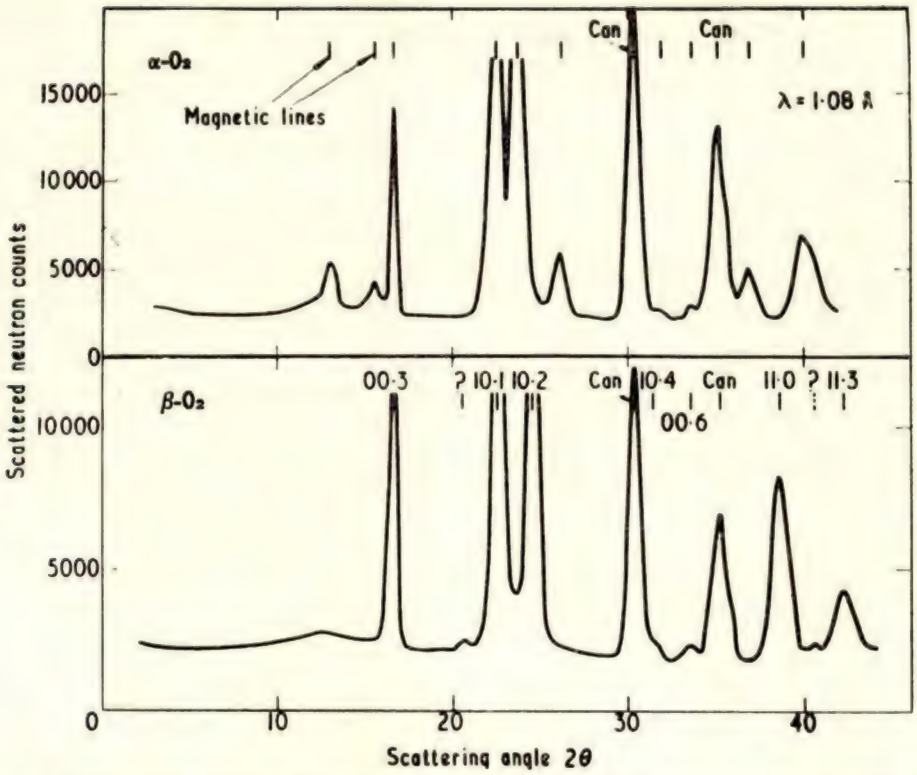

Fig. 6. Neutron powder patterns from $\alpha - O_2$ (= III) at 4.2K and from $\beta - O_2$ (= II) at 27K. The first two lines from $\alpha - O_2$ are not observed on X – ray powder photographs, and indicate the presence of an ordered antiferromagnetic structure. The broad peak in the diffuse scattering from $\beta - O_2$ at a scattering angle of about 12° indicates short range antiferromagnetic order between the spins.

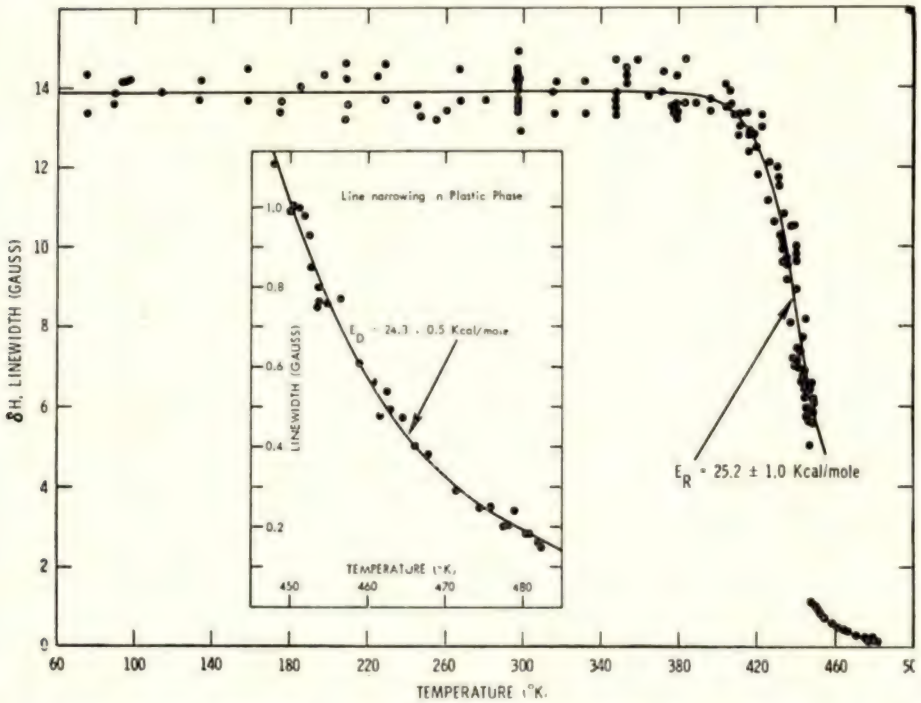

Fig. 7. Proton magnetic resonance linewidth, δ H, against temperature for pentaerythritol, $C(CH_2OH)_4$. The temperature of the transition to the plastic phase is about 457K. The part of the curve for the plastic phase is shown in the inset on an enlarged scale. E_R and E_D are the estimated activation energies for reorientational and diffusion of the molecules respectively.

-red (the region where intra-molecular vibration frequencies characteristically reveal themselves) and in the far infra-red. The latter region is being increasingly used now that the technical diffilculties have been largely overcome, and is particularly informative since it provides a means of getting direct information on the frequencies with which molecules rock (that is, undergo torsional oscillations) in the lattice. Generally speaking, both the near and far infra-red spectra of an ordered crystal show more detail or structure than that of the same substance in a disordered state. This is because the environment of a molecule or ion in the ordered crystal will be more regular or uniform than that for a disordered crystal, in which the environment will tend to vary at any instant from one molecule to another, so that the observed spectrum will represent an average state of affairs. This point is illustrated by Fig. 8, which are shown the far infra-red spectra of the three forms of DBr[20], already mentioned in Section A(2). The spectrum of the ordered form III reveals both lattice vibration frequencies (the two peaks at the lowest frequencies) and torsional oscillational frequencies (the two central peaks). In the partially disordered form II, there is less structure, but the lattice vibration frequencies are still visible, while the still more disordered form I has a much more diffuse spectrum, rather like that of a liquid. In Fig. 9, part of the near infra-red spectrum of one of the high-pressure forms of ice, namely II, is compared with that of form I (the form stable at ordinary pressures) and forms III and V.[21] In I, III and V the protons are positionally disordered, whereas in II they are ordered. Again, it will be seen that the spectrum whith the most structure is that of the ordered form II.

Rather less use has been made of Raman spectra, but the spectrum of crystalline hydrogen within a few degrees of its melting-point supplied an elegant proof of the statement made earlier (Section A (2)) that this is a rare example of a lattice in which molecules can really rotate freely.[22] The Raman spectrum of para-hydrogen (for the molecules of which the rotational quantum number, J, = 0,2,4, ...) shows a line with $\triangle = 355.5$ cm^{-1}, while that of normal hydrogen (consisting of $\frac{3}{4}$ ortho-hydrogen and $\frac{1}{4}$ para-hydrogen) gives this line and one with $\triangle = 589$ cm^{-1}. These two frequencies are almost exactly those for the rotational transitions $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$ respectively, being virtually identical with the corresponding Raman frequencies for the molecules in the gaseous state.

(6) *Magnetic susceptibility studies.* In addition to the neutron diffraction studies already mentioned, the temperature dependence of the magnetic susceptibility χ can give valuable information on the type of magnetic ordering ultimately adopted on cooling a paramagnetic

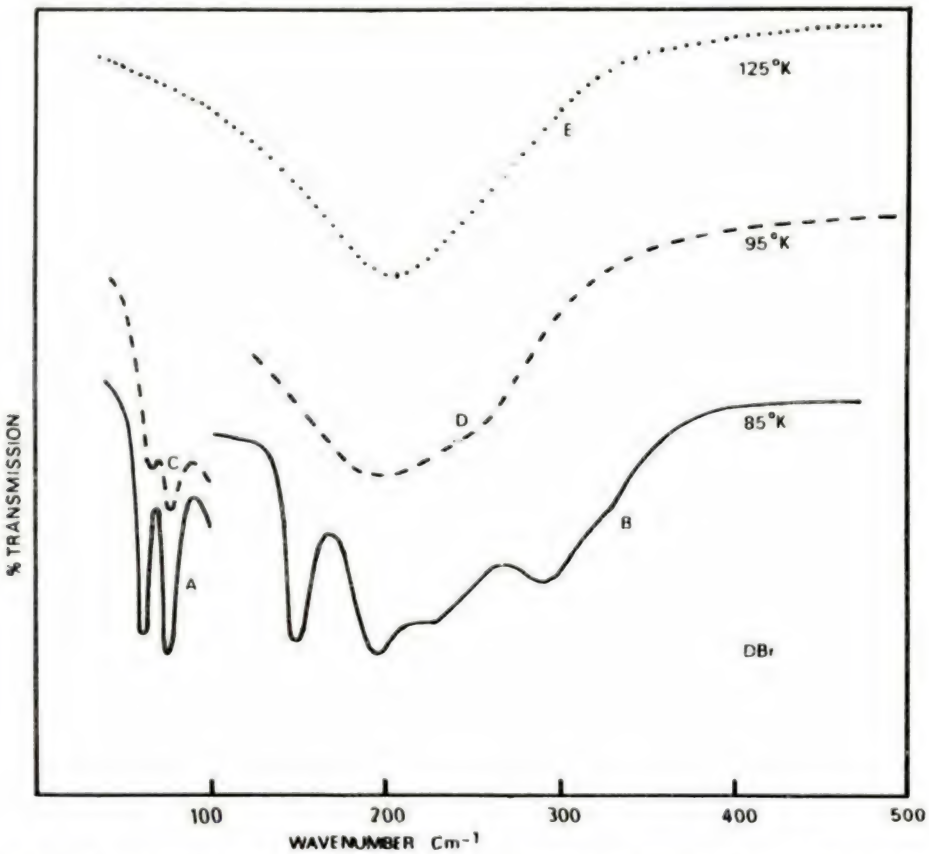

Fig. 8. The far infra-red spectra of solid DBr. A and B, phase III at 85K. C and D, phase II at 95K. E, phase I at 125K.

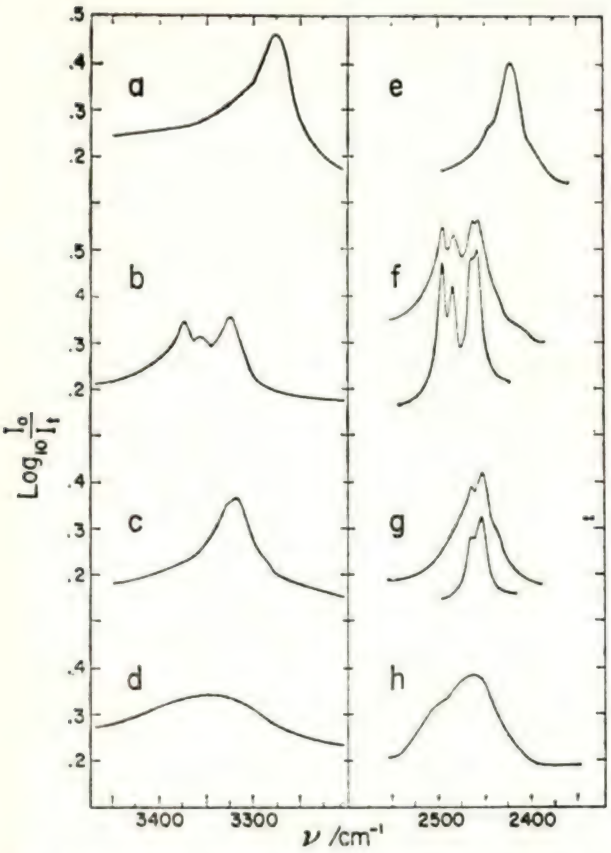

Fig. 9. ν_{OH} (HDO) and ν_{OD} (HDO) in various phases of ice as mulls in isopentane at ~ 100°K. The ices used were: Curve a; Ice Ih, 95% D_2O 5% H_2O: Curve b; Ice II, 95% D_2O 5% H_2O: Curve c; Ice III, 95% D_2O 5% H_2O: Curve d; Ice V, 95% D_2O 5% H_2O. Curve e; Ice Ih, 95% H_2O 5% D_2O. Curve f upper; Ice II, 95% H_2O 5% D_2O: Curve f lower; Ice II, 99% H_2O 1% D_2O: Curve g upper; Ice III, 95% H_2O 5% D_2O: Curve g lower; Ice III, 99% H_2O 1% D_2O: Curve h; Ice V, 95% H_2O 5% D_2O. The lower curve in f is plotted 0.05 units lower than observed, and curve h is plotted 0.1 units higher than observed.

crystal. The characteristic dependence of χ on T, depending on whether the solid becomes ferromagnetically or antiferromagnetically ordered, is shown in Fig. 10.

(7) *Slow neutron scattering studies.* This is an interesting technique, likely to be put to increasing use in studying disordered crystals. Neutrons from an atomic pile are slowed down until their energies are comparable with the energies associated with the vibrations and torsional oscillations of the molecules in the lattice. Changes in the energy of the neutrons in the beam on passage through the crystal can therefore give information on the movement of the molecules. An example of this will be found in recent work on methane.[23]

(8) *Radiotracer techniques.* Some use has been made of these for obtaining information on the kinetics of the movement of molecules from site to site in a lattice, as for example in the high-temperature disordered phase of cyclohexane (the so-called plastic crystalline phase).[24]

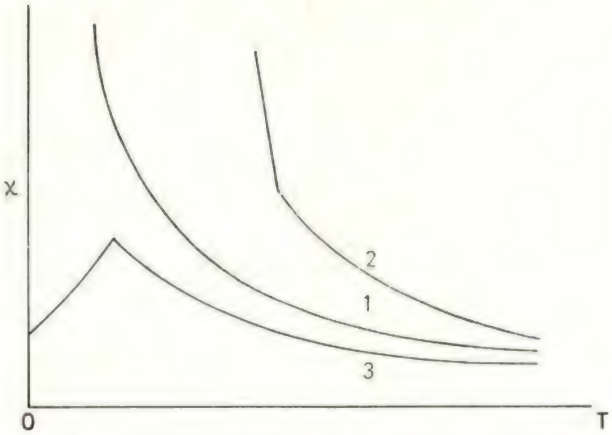

Fig. 10. Illustrating the characteristic dependence on temperature T of the magnetic susceptibility χ of a paramagnetic solid (1), a solid which becomes ferromagnetically ordered (2), and a solid which becomes antiferromagnetically ordered (3).

D. THEORETICAL ASPECTS

In a general review of this kind it is impossible to deal adequately with the very considerable amount of theoretical work carried out on order-disorder problems in crystals, but attention will briefly be drawn to some of the aspects of the subject which theoretical treatments must consider. The equilibrium condition of a crystal is determined by the balance between two opposing factors. One of these is thermal agitation, whith tends to produce a disordered state, The other is the interaction between the particles in the lattice, which tends to order the particles in a way which will minimize the energy of the system. The theoretical investigation of the balance reached at a given temperature between these opposing factors is a matter for statistical mechanics. In general, different arrangements or different mutual orientations of the particles in the lattice will mean different energies, and to deal with these some assumption has to be made about the way the particles interact, that is to say some 'model' has to be adopted. Almost always the model is a simplification of the true state of affairs. One of the best known is the Ising model, originally introduced to deal with magnetic interactions, but now used in a more general way (ses, for examples references 25 and 26. This at first sight seems a very simple kind of interaction, but even so its use can lead to mathematics of great complexity.) Sometimes the energy differences are small enough for them to be disregarded to a first approximation, but this can still leave 'configurational problems', for example problems of the number of possible distinguishable ways of distributing particles on a lattice. These, too, can be of considerable difficulty. A famous calculation by Pauling[27] of the number of acceptable ways W of distributing the 2N protons in a mole of ordinary ice gave the answer $W = (3/2)^N$. But it is now known that this is not quite exact, though the value of $k\ln(3/2)^N$, $= R\ln(3/2)$ which it gives for the residual molar entropy of ice is believed to be correct to within about one per cent. (An exact value for W has

not yet been obtained, but a very good estimate is considered to have been reached by computation)[28]. Another configurational problem is the so-called dimer problem. Imagine a primitive cubic lattice, which is to be occupied in a disordered way with dimers, that is rod-like particles the two ends of which occupy two adjacent cube corners. In how many ways can the dimers be fitted into the lattice? This problem has also so far resisted exact solution.

With regard to the forces responsible for the ordering of a lattice at sufficiently low temperatures, the nature of these must naturally change from one type of crystal to another. Thus, that the FeAl alloy becomes ordered in the way described in Section A(1) must mean that Fe-Al interactions are energetically preferred compared with Fe-Fe and Al-Al interactions. It might be supposed that orientational order in a simple polar diatomic substance like HCl or DBr is due to dipole-dipole interaction, and this may be so, but it is interesting that in the low-temperature ordered forms of these halides the adjacent molecules in the chain (see Section A(2)) are at about 90° to each other, which is not the arrangement which gives the strongest electrostatic attraction between dipoles. It implies rather that the attraction arises between the positive charge on the hydrogen atom and an unshared pair of p-electrons on the halogen atom, so that it may perhaps be regarded as a case of hydrogen bonding. In the orientationally ordered forms of some well-known diatomic substances (H_2, N_2, CO, F_2) there is little doubt that the ordering force is that between the molecular quadrupoles. The charge distribution is such that a molecule may be represented thus:

and an energetically preferred orientation between two such quadrupoles is the following:

In their low-temperature ordered forms, all the four diatomic substances just mentioned have a cubic lattice made up of four sub-lattices, arranged so that this energetically favourable orientation can contribute to the stability of the lattice. It is significant that this structure is the same as that of solid CO_2, the molecule of which has a relatively large quadrupole moment. In solid tetrahydrides such as CH_4, CD_4, and SiH_4, the symetry of the molecules is so high that the 'first' electrical moment the molecule possesses is an octupole moment, which is considered to be responsible for the orientationally ordered low-temperature forms of these substances.

In magnetically ordered solids, the forces producing the order are of yet another kind. The magnitude of these forces in, for example, transition metal oxides, sulphides and halides generally proves to be greater than one might expect if the transition metal ions merely affected each other as if they were magnets interacting through space, and it is generally believed that interaction is transmitted through the electronic system of the intervening anions by a form of electron delocalization, or covalency, called 'superexchange'[29]. So one consequence of the study of magnetic order-disorder transitions is that something may be learnt about the electronic structures of the solids concerned.

E. ORIENTATIONAL DISORDER AND ENTROPY

It is sometimes possible (though by no means always) to interpret the entropy gain associated with an order-disorder transition on the basis of the well-known equation:

$$S = k \ln w,$$

where k is the Boltzmann constant and w is the number of microstates (sometimes called the number of complexions) for the system.[30, 31] Thus, if a diatomic or polyatomic ion or molecule goes from a condition in which it has n_1 distinguishable orientations to one in which it has a larger number n_2 of distinguishable orientations, the entropy gain per mole of the molecule or ion on this account (assuming that at any instance the ion or molecule can make full use of the orientations available to it) is $k \ln(n_2/n_1)^N$, $= R \ln(n_2/n_1)$. (The phrase 'on this account' is inserted because simultaneously with the gain in orientational disorder there may be a crystal structure change, or at least a volume change, as a result of which the vibrational frequency spectrum of the lattice alters, so that there is also a change in the vibrational entropy of the crystal. Generally speaking, such secondary contributions to the entropy change will be less, the less the difference between the crystal structures of the ordered and disordered forms). In the case of the λ-transition in ammonium chloride, in the low-temperature ordered form all the tetrahedral ammonium ions have one and the same orientation — they are all parallel to one another — so that $n_1 = 1$, whereas in the disordered form $n_2 = 2$, and hence the entropy gained on this account is R in2, = 1.38 cal mol^{-1} K^{-1}. This agrees with the experimental figure within the precision with which it can be measured.[32] The lower transition III → II in KCN (Fig. 3) involves no change in the orthorhombic crystal structure, and since the measured entropy gain of 1.32 cal mol^{-1} K^{-1} is close to R ln2, it is probable that each CN^- ion in the low-temperature form III has a definite orientation ($n_1 = 1$), whereas in II it has two possible orienta-

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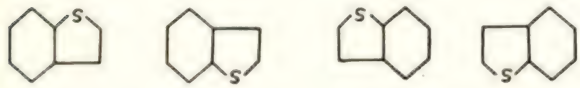
tions, CN^- or NC^-, ($n_2 = 2$), — sometimes referred to as 'head-to-tail' disorder. In the face-centred cubic lattice I where each CN^- ion has six K^+ neighbours, it is likely that it has six possible orientations, so that the entropy gain at the II → I transition due to the increase in the number of possible orientations for each anion from two to six is R ln3, = 2.18 cal mol^{-1} K^{-1}. The experimental value[9] is 2.01 ± 0.03 cal mol^{-1} K^{-1}.

The substance benzthiophene[33] has a λ-type transition just below room temperature, at which the entropy gain is 2.75 cal mol^{-1} K^{-1}. This is almost exactly R ln4, which implies that while below the λ-transition all molecules have a unique orientation in the lattice, above the transition each molecule makes use of four possible orientations, as follows:



Nevertheless, it must not be supposed that the entropy changes of all order-disorder transitions, especially when they are first-order, can be so simply explained. Thus, the II → I phase change in HCl and DCl almost certainly takes the molecules from a lattice in which they each have a unique orientation to one in which they have twelve possible orientations. But the entropy gain at this transition is not R ln12, = 4.94 cal mol^{-1} K^{-1}, but only 2.89 cal mol^{-1} K^{-1}. This 'discrepancy' is no doubt partly due to the fact that there is a crystal structure change and therefore some change in the contribution which the lattice vibrations make to the total entropy. But in addition a molecule in the high-temperature form cannot choose which of its twelve possible orientations it will adopt independently of the orientations its neighbours may happen to have at that moment, since this would sometimes lead to the arrangement Cl — H... H — Cl, which is virtually impossible because of the repulsion between the hydrogen atoms.

It is characteristic of the structure of a salt that the cations and anions are arranged in alternate shells, so that if for example the anions are monatomic while the cations are diatomic or polyatomic, the latter are, as it were, protected to some extent from each other by an intervening shell of anions. This might be expected to reduce somewhat the sort of mutual interference which we have just illustrated by the example of HCl-I, and therefore one might predict that the entropy gains associated with the transitions in salts involving orientational disorder would more nearly be given by R lnx, where x is a relatively small integer or a simple fraction. This is indeed found.[34] Fig. 11 is essentially a represen-

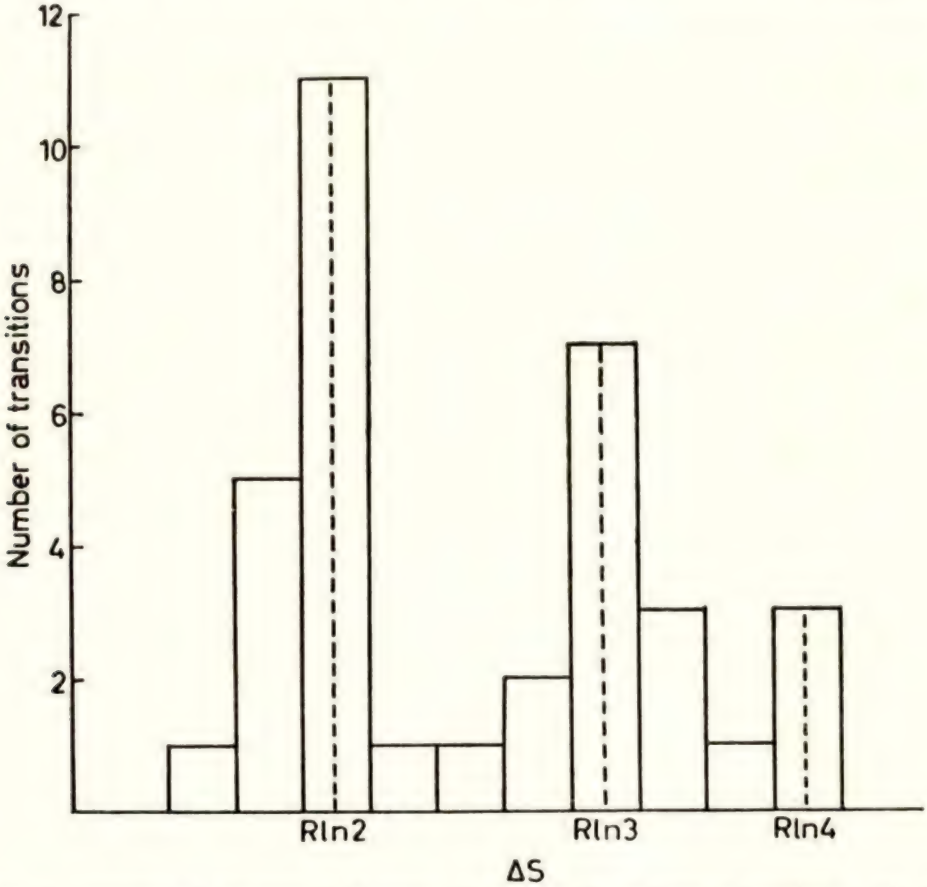


Fig. 11. Distribution of the values of the entropy of transition ΔS for thirty-five transitions in salts for which ΔS lies between 0.8 and 3 cal mol^{-1} K^{-1}. The width of each colum is 0.2 cal mol^{-1} K^{-1}

tation of the distribution of 35 experimental values of transition entropies in salts. The grouping of these values round R ln2 and R ln3, and to lesser extent round R ln4, is striking.

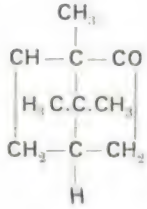
When a crystal remains in a disordered state down to OK, the value of the residual entropy S_{res} can often be interpreted on the basis of the expression k lnw. Crystalline N_2O is an example.[35] The molecules are linear, and apparently disordered as between the two possible orientations NNO and ONN. If the disorder were complete we should expect that S_{res} would be R ln2, = 1.38 cal mol^{-1} K^{-1}. In fact, the experimental value (as given by $S_{spec} - S_{cal}$) is a little less than this, being 1.14 cal mol^{-1} K^{-1}, implying that there is some degree of local order, that is, that there is a slight preference for the neighbours of a given molecule to have one of the two possible orientations rather than the other. Crystalline nitric oxide, NO, presents an interesting case of residual disorder.[36] The crystal is diamagnetic, unlike the liquid and gas, and the unit in the lattice is a dimer, N_2O_2 . The mole of NO provides N/2 dimers, and the assumption that each dimer has two possible orientations leads to the prediction that S_{res} should be k $\ln 2^{N/2}$, = R/2 ln 2, = 0.69 cal mol^{-1} K^{-1}. The experimental value, i.e. $S_{spec} - S_{cal}$, is 0.72 cal mol^{-1} K^{-1}.

F. PLASTIC CRYSTALS

This name has been given to a type of disordered molecular crystal (usually, though not always, of an organic compound) with relatively small entropies of fusion (usually less than 5 cal mol^{-1} K^{-1}).[37] Table 1 gives a few examples of substances which form plastic crystals. (Some of the simple substances we have already mentioned, for example N_2 ,F_2 and CH_4 , could also legitimately be described in their disordered phases as plastic crystals). A more complete list has been given by Timmermanns[38], who first recognized the existence of this interesting type of crystal. He noted that the molecules forming them tended to be approximately spherical, including for example, tetrahedral molecules like neopentane ($C(CH_3)_4$), cyclic molecules like cyclohexane, or cage molecules like camphor, and he proposed the term 'globular molecules' to describe them. The plastic crystal is formed from a low-temperature phase at a transition which may be first-order or λ-type

TABLE 1

Some examples of plastic crystals, showing: (1) the temperature at which the plastic phase is formed from the 'ordinary' low-temperature phase: (2) the melting-point of the plastic phase; (3) the corresponding entropies of transition and fusion, (all △S values in cal mol^{-1} K^{-1}); (4) for the first four examples, the nature of the transition. (F = first-order transition, λ = gradual transition, for which the transition temperature is that at which the heat capaciy is a maximum).

		II ←	I ←	LIQUID
		'Ordinary' phase	'Plastic' phase	
Carbon tetrachloride	CCl_4	225.5K(F) △S = 4.86	250.3K, △S = 2.40	
Carbon tetramethyl	$C(CH_3)_4$	140K(λ) △S = 4.39	256.5K, △S = 3.03	
Pentaerythritol	$C(CH_2OH)_4$	457K(F) △S = 22.8	539K, △S = 3.16	
Cyclohexanol	$C_6H_{11}OH$	265.5K(F) △S = 7.95	299K, △S = 1.4	
Camphor		250K, △S = 7.6	453K, △S = 2.8	
Tungsten hexafluoride	WF_6	265°K, △S = 7.8	275°K, △S = 3.56	

and at which there is a considerable entropy increase, greater than that which accompanies the melting of the plastic crystal. The difference between $\triangle$ S(transition) and $\triangle$ S(fusion) for pentaerythritol, (Table 1) is a striking example of this. Sometimes the entropy of fusion of the plastic crystal is surprisingly small; that of cyclopentane is only 0.80 cal mol^{-1} K^{-1}. The range of existence of the plastic crystalline phase can vary considerably. Thus, in the examples given in Table 1, it is only about 10° for WF_6, but over 200° for camphor.

A feature of plastic crystals is that they give rather poor, indistinct X−ray diffraction patterns, but these when analyzed usually reveal that the plastic phase is one of high symmetry. Thus, the plastic crystalline phase of cyclobutane only gave two usable lines in its X−ray powder photograph, just sufficient to show that its lattice is body-centred cubic.[39] The low entropies of fusion and the rather blurred X−ray diffraction patterns are evidence that the crystals are highly disordered, and this is amply confirmed by NMR studies. An example of the line narrowing associated with a plastic crystal has already been given in Fig. 7 for pentaerythritol. The line-width just below the melting--point of a plastic crystal is often almost as small as that for a liquid. In general, it may be said that in a plastic crystal the molecules have considerable orientational disorder, and also the ability to move easily from one lattice site to another. This ease of movement probably depends on the fact that the crystal has developed an appreciable fraction of unoccupied sites (Schottky holes), so that a molecule can relatively easily leave its site and move into a hole, leaving a hole behind it which another molecule can use, and so on. In principle, the fraction of such holes can be estimated by comparing the actual measured density of the crystal with that calculated from the lattice spacing given by an X−ray study, since the presence of holes will mean that the actual density will be less than the calculated density. It has been found in this way that the percentage of unoccupied sites in a plastic crystal does not usually exceed one per cent,[40] but an exception is provided by the plastic crystalline phase of the hydrocarbon camphene, in which it has been estimated that about seven per cent of the lattice sites are unoccupied at the melting-point.[41]

The adjective 'plastic' reflects the fact that many such crystals can be extruded through holes by relatively low pressures, (e. g. pressures of a few hundred atmospheres).[38] The plastic crystalline phase of perfluorocyclohexane, C_6F_{12}, is said to flow slowly under gravity, like pitch. The plasticity of these peculiar crystals may well depend, like the ease of diffusion of the molecules, on the Schottky holes in the lattice.

It may be noted that the well-known use of camphor as a cryoscopic solvent for molecular weight determinations depends on its existence as a plastic crystal. Since the entropy of fusion and the heat of fusion $\triangle H_f$ are relatively low, the cryoscopic constant (which is inversely proportional to $\triangle H_f$) is large, and a relatively large depression of the freezing-point of camphor is produced by a relatively low concentration of a solute.

G. DISORDER OF POSITION

In Section A(1), ordinary ice (that is, the hexagonal form stable at ordinary pressures) was mentioned as an example of positional disorder. In addition to this stable form, there is an unstable cubic form (also disordered with regard to the protons), and no less than eight high-pressure forms. Of these, it appears that three have the protons in an ordered arrangement, while the rest are disordered. The three ordered forms are II, and forms VIII and IX which have only comparatively recently been discovered. One simple thermodynamic piece of evidence[42] that II is an ordered structure may be mentioned here. From the pressure − temperature phase diagram for the ice system (our knowledge of which is largely due to the work of Bridgman, supplemented later by the work of Whalley and his associates),[43] estimates can be made of dp/dT, the slope of the line for the co-existence of two phases, such as III and V. The volume change $\triangle$ V for the conversion III $\rightarrow$ V can be measured directly, so from dp/dT, $\triangle$ V and the Clapeyron equation

$$dp/dT = \triangle S / \triangle V$$

a value is obtained for $\triangle$ S for the process III$\rightarrow$V. It is found in this way that for all possible conversions of one phase into another for the forms of ice from I to VII, those conversions which do *not* involve II have only small entropy changes, averaging numerically about 0.07 cal mol^{-1} K^{-1}. But when II is converted into any one of the three phases which are its neighbours on the phase diagram, namely I, III and V, (IV is a metastable phase), $\triangle$ S is much larger, being (in cal mol^{-1} K^{-1}) 0.8 for II $\rightarrow$ I, 1.0 for II $\rightarrow$ III, and 1.0 for II $\rightarrow$ V. Since the entropy which ordinary disordered ice-I retains at 0K is 0.80 cal mol^{-1} K^{-1}, the inference is clearly that II is an ordered state, while III and V, like I, have a disordered arrangement of protons. This conclusion about II is confirmed by its infra-red spectrum (mentioned in Section C(5)), and by other properties such as its dielectric constant.[44]

Since ordinary ice is disordered at all temperatures, it is natural that studies should have been made of crystals containing water of crystallization to see if they are similar. Experimentally, this is a matter of using the procedure outlined in Section B(2), that is of comparing the apparent calorimetric entropy of the hydrate, S_{cal}, with S_{eq}, the value obtained by an equilibrium study. Thus, for Na_2SO_4, 10 H_2O,[45] S_{eq} can be obtained from the equilibrium:

$$Na_2SO_4, 10H_2O\ (c) = Na_2SO_4\ (c) + 10\ H_2O\ (g).$$

If the water vapour dissociation pressure at, say 25°C is p_{H_2O}, then $\triangle G^\circ = -RT\ln p_{H_2O}$[10]. The standard enthalpy increase for the reaction, $\triangle H^\circ$, can be obtained from the heat of vaporization of water and the heats of solution of the anhydrous Na_2SO_4 and the hydrate, (strictly, to give very dilute solutions). $\triangle S^\circ$ for the reaction then follows from the relation

$$\triangle G^\circ = \triangle H^\circ - T\ \triangle S^\circ.$$

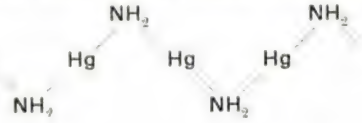
Using appropriate heat capacity results, the $S_{Na_2SO_4}$ the molar entropy of the anhydrous salt is determined from the integral $\int C_p/T.dT$, (since there is no reason to suppose that the anhydrous salt will be disordered in any way at OK), while $S^\circ_{H_2O}$, the molar entropy of water vapour at one atmosphere and 25°C, is accurately known. S_{eq}, the true entropy of the decahydrate, then follows from the equation:

$$\triangle S^\circ = S_{Na_2SO_4} + 10\ S^\circ_{H_2O} - S_{eq}$$

S_{eq} was found in this way to be 141.46 cal mol^{-1} K^{-1}, whereas S_{cal}, the apparent calorimetric entropy, is only 139.95 cal mol^{-1} K^{-1}. So S_{res} is 1.51 cal mol^{-1} K^{-1}, and hence the hydrate remains disordered at OK. It will be noted that S_{res} is only about one per cent of S_{eq} and S_{cal}, so that very accurate work is essential. A crystal structure study of the decahydrate[46] suggests that some of the protons of the water molecules in the lattice have definite positions, but that for every mole of salt there is a group of four water molecules arranged in a ring, and the fact that S_{res} is approximately R ln2 suggests that there are two ways in which the protons in the ring can be arranged, as shown in Fig. 12. Two other disordered hydrates are $Na_2CO_3,10H_2O$[47] (S_{res} = 1.50 cal mol^{-1} K^{-1}) and $Na_2HPO_4,12H_2O$,[48] (S_{res} = 3.51 cal mol^{-1} K^{-1}). But most hydrates which have been studied in this way (mostly by Giauque and his collaborators) prove to be ordered. They include the following: five hydrates of H_2SO_4; three hydrates of NH_3; two hydrates of HNO_3; the hydrates of NaOH; $ZnSO_4,7H_2O$; Na_2CO_3,H_2O; $Na_2HPO_4,2H_2O$ and $7H_2O$.

An interesting and much studied hydrogen-bonded crystal is that of KH_2PO_4. This exists in an ordered, orthorhombic form II and a high-temperature disordered form I, the two being separated by a λ-type transition with its heat capacity maximum at ≈ 123K. There is a similarity here, perhaps at first sight unexpected, with ice-I. The structure of ice is determined by the fact that each water molecule has two protons for forming hydrogen bonds and two lone pairs of electrons for attracting the protons of other molecules, the two protons and the two lone pairs of a given molecule being approximately tetrahedrally disposed. Similarly, the anion in KH_2PO_4, namely $\begin{matrix} HO\backslash & /O \\ & P \\ HO/ & \backslash O \end{matrix}$, has two protons, and two oxygen atoms to attract protons, again approximately tetrahedrally disposed. Whereas, however, in ice, the disordered hydrogen-bonded structure persists to OK, in KH_2PO_4 it gives place to an ordered arrangement below the transition. The entropy lost when I transforms into II on cooling is 0.74 cal mol^{-1} K^{-1}.[49] which within experimental error is the same as S_{res} for ice. It then seems that as a consequence of the ordering of the hydrogen bonds, slight changes in position of the other atoms (e. g. the potassium ions) take place, as a result of which a unit cell develops a dipole moment. Since the structure is ordered, the dipole moment of the cells of a group or domain all have the same direction, so that the domain of cells is polar. This confers on the ordered crystal an exceptionally high dielectric constant (~ 10^4); in other words, it belongs to the interesting and important class of solids known as ferroelectrics.[50]

An example of positional disorder which can be described as 'random walk disorder' has recently been investigated by Mr. R. D. Worswick in the author's laboratory. This occurs in the substance mercury (II) amidobromide, $HgNH_2Br$, which can be obtained in two forms, an orthorhombic form and a cubic form.[51] The cubic form is unstable at room temperature, but the rate of change into the orthorhombic form appears to be so slow that no transformation can be observed over a period of months. The cations in both forms consist of chains



in which the unit N—Hg—N is linear. In the orthorhombic crystal, the Hg and N atoms of any cation chain lie in a plane, forming a regular zig-zag, and adjacent chains are parallel so that all Hg atoms have definite positions. In the cubic form, the N atoms lie at the cube corners, and every Hg atom must be situated half-way between two N atoms, that is at the mid-points of the cube edges.

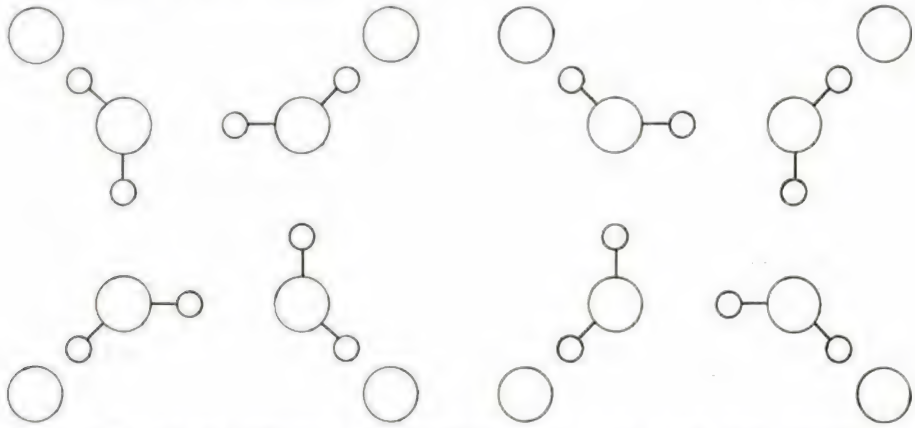


Fig. 12. Showing the two possibilities for hydrogen-bonding in a ring of four water molecules in the lattice of Na_2SO_4, $10H_2O$. The larger circles are oxygen atoms, the smaller circles are hydrogen atoms.

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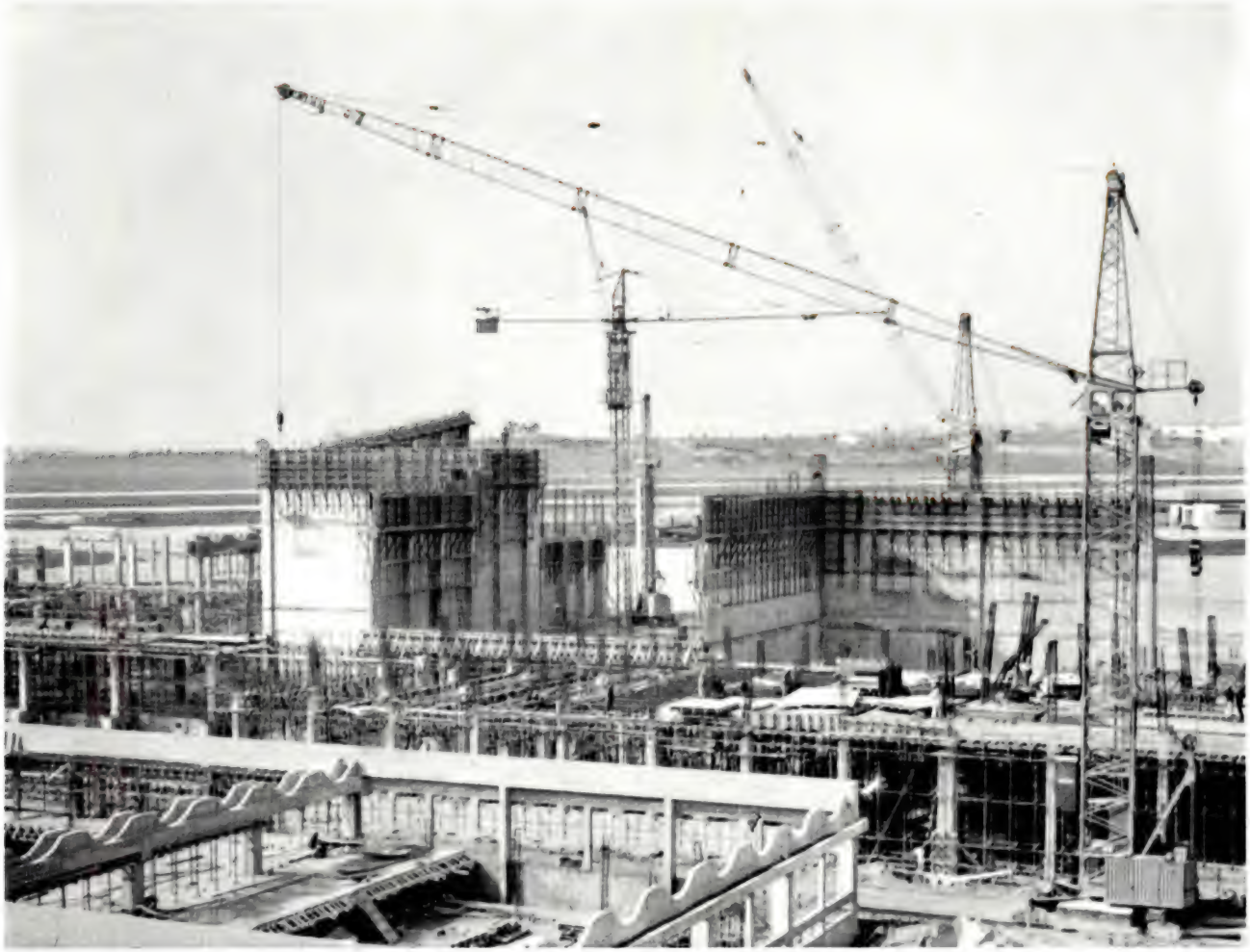
6 DELEGAÇÕES NA METRÓPOLE E ULTRAMAR

CONSTRUÇÕES TÉCNICAS, LDA.



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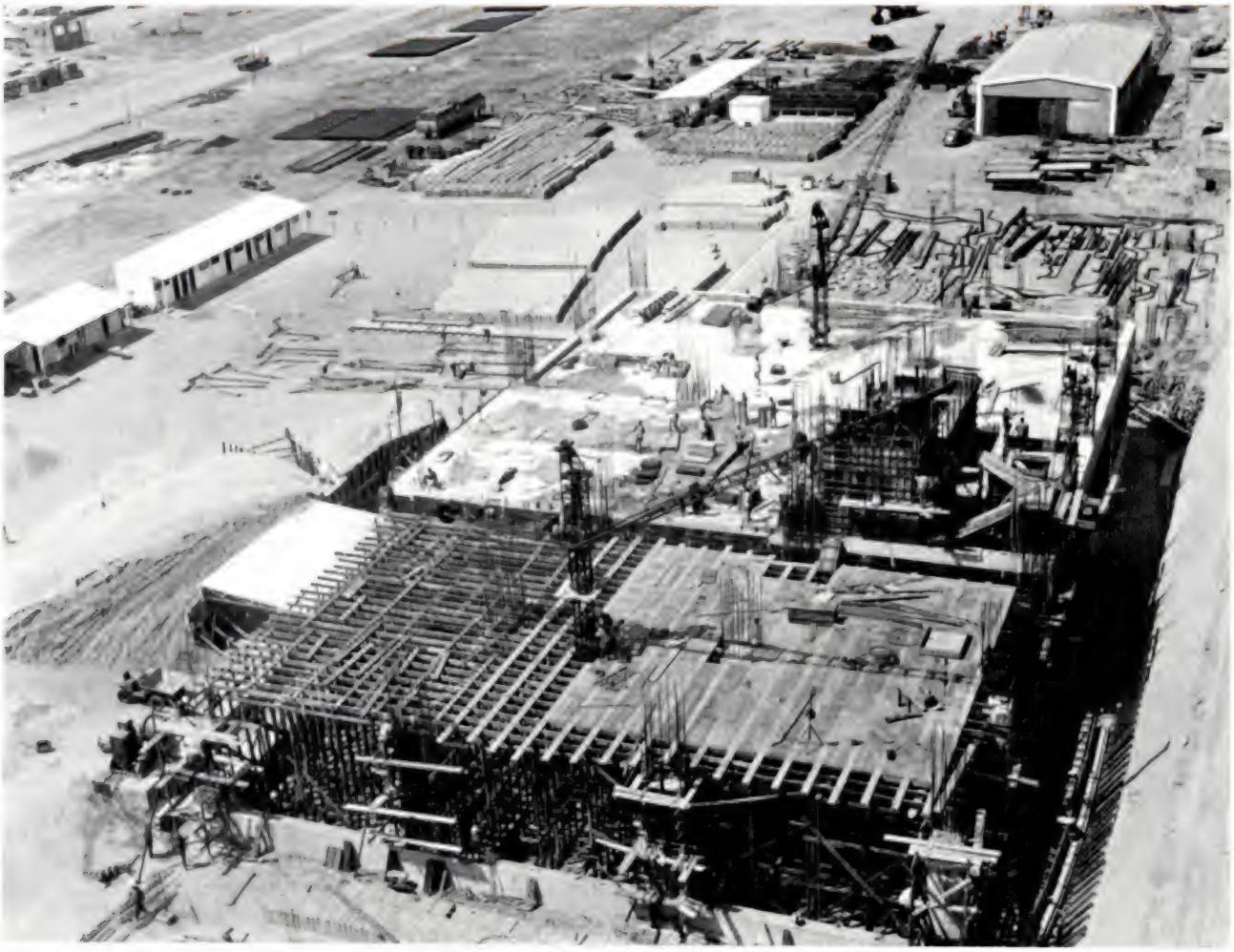

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Only one-third of these possible sites for the Hg atoms is occupied, however, so that the Hg atoms are positionally disordered. This is equivalent to saying that the path taken by a cation chain in the cubic form is a path followed on a walk through the cubic lattice in which every step (i. e. an N—Hg—N unit) is an edge of a cube, and in which each step must be at 90° to the preceding step. The determination of the number of such walks which are possible in a given crystal is another example of a configurational problem which cannot be exactly solved, but an approximate estimate has been made by Dr. D. F. Mayers by computing the number of random walks possible for blocks of unit cells of increasing size, beginning with 3x3x3. The computation has been carried as far as blocks of 13x13x13 unit cells, (the computing time required rising rapidly, of course, with increasing size of the block). Extrapolation of the results so obtained to (in effect) the infinitely large crystal, gives an estimate of about 1.7 cal mol^{-1} K^{-1} for the entropy associated with 'random walk disorder' in a mole of Hg NH_2 Br. The experimental examination of whether or not the crystal retains entropy of about this amount at OK has been made by comparing its apparent calorimetric entropy S_{cal} at 25°C with S_{eq}. S_{eq} was determined by measuring the molar entropy at 25°C of the orthorhombic form, S_{or}, and also the difference $S_{or} - S_{eq}$. This difference was determined with the help of the cell

$$\mathrm{Hg} \,|\, \underset{\text{(cubic)}}{\mathrm{HgNH_2\,Br\ (c)}} \,|\, \mathrm{KBr\ (aq)} \,|\, \underset{\text{(orthorh.)}}{\mathrm{HgNH_2\,Br\ (c)}} \,|\, \mathrm{Hg},$$

in which the cell 'reaction' is

$$\mathrm{HgNH_2\,Br\ (cubic)} = \mathrm{HgNH_2\,Br\ (orthorhombic)}.$$

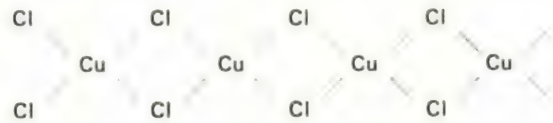
This cell gave a fairly reproducible E. M. F. of 0.0050 volts, which corresponds to $\triangle G^\circ = -230$ cal mol^{-1}. $\triangle H^\circ$ for the cell reaction was found to be -15.5 cal mol^{-1} from the difference in the heats of solution of the two crystalline forms in hydrochloric acid. These results give $\triangle S^\circ = S_{or} - S_{eq} = 0.72$ cal mol^{-1} K^{-1}. S_{cal} for the cubic and orthorhombic forms were determined by appropriate low-temperature calorimetry to be 31.31 and 31.83 cal mol^{-1} K^{-1} respectively. S_{res} for the cubic form then follows from the equation

$$S_{res} + 31.31 + 0.72 = 31.83,$$

giving $S_{res} = -0.20$ cal mol^{-1} K^{-1}, with an estimated uncertainty of $\pm$ 0.3 cal mol^{-1} K^{-1}. Therefore S_{res} is zero within experimental error. This is a somewhat surprising result, since it means that the cubic form, while undoubtedly disordered at room temperature, somehow contrives to become ordered (as regards the position of the Hg atoms) on cooling, although there was no sign of any transition in the heat capacity measurements, which extended from ~ 10K to 300K.

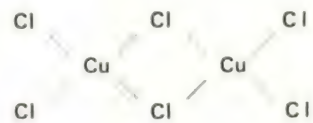
H. MAGNETIC DISORDER

This is a large subject, and we shall limit ourselves to a brief illustration of a point not so far made, namely that the order-promoting influence in a crystal may be much stronger in one direction than in another. Consider, for example, a copper (II) compound. The ion Cu^{2+} with a $3d^9$ structure has one unpaired electron, so that the degeneracy which can result from the spin of $S = \frac{1}{2}$ is $2S + 1, = 2$, and the total magnetic entropy gained by the spin system becoming disordered is therefore R ln2. The ordering at sufficiently low temperatures can be antiferromagnetic or ferromagnetic. In Cu Cl_2, the transition from the antiferromagnetically ordered state to the disordered state gives a pointed maximum in the heat capacity at about 24K.[52] At this temperature, however, only about 27 per cent of the magnetic entropy of R ln2 has been acquired. Analysis of the heat capacity shows that the rest of the magnetic entropy is developed between 24K and about 100K. This is readily interpreted in terms of the crystal structure of $CuCl_2$, which consists essentially of parallel chains:



The magnetic interaction between the copper atoms along the chain is much stronger than that between copper atoms of different chains. At sufficiently low temperatures the system is magnetically ordered in three dimensions, but the magnetic order between the chains is relatively easily broken down, while leaving considerable order along the chains which finally disappears only at much higher temperatures. This is no doubt a case where the interaction between the copper atoms, particularly along the chains, depends on superexchange (Section D).

We have recently investigated magnetic transitions in double copper chlorides containing the anion $Cu_2\,Cl_6^{=}$, of structure



An example of such a salt is Li Cu Cl_3, 2 H_2O, which undergoes a gradual antiferromagnetic $\rightarrow$ paramagnetic transition with a maximum in the heat capacity at about 4K.[53] The entropy gain associated whith this transition was found to be 1.07 ± 0.02 cal mol^{-1} K^{-1}, which is less than R ln2, but significantly, almost equal to $\frac{1}{2}$ R ln3. The interpretation of this result is that the two spins of the copper atoms within one and the same anion are strongly coupled in a parallel way, giving a resultant spin $S = 1$, and a degeneracy of 3. There are N/2 anions per mol of the double chloride, so if it is supposed that above 4K the magnetic order between the anions has disappeared (while the coupling between the two copper atoms in any one anion still persists), the expected magnetic entropy gain shoul be k ln $3^{N/2}$, $= \frac{1}{2}$ R ln3, in agreement with the experimental result.

Thus the conclusion reached from this simple thermodynamic observation is that in the $Cu_2Cl_6^{=}$ ion, the superexchange is of a kind which produces a relatively strong interaction between the copper atoms, resulting in parallel spins of the unpaired electrons.

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FEIRAS, CONFERÊNCIAS, EXPOSIÇÕES E CURSOS NO MUNDO

A ENGENHARIA SANITÁRIA E O ENSINO

Organizada pela Comissão de Engenharia Sanitária da Ordem dos Engenheiros decorreu, no mês de Novembro de 1971, no colóquio versando diferentes temas relacionados com o saneamento do meio urbano, e controlo da poluição industrial. Um dos subtemas mais aliciantes do referido colóquio terá sido o «Ensino». Discutiu-se a necessidade de uma educação sanitária da população; focaram-se os problemas da participação consciente da comunidade, e da formação de especialistas, através de cursos de reciclagem e de pós-graduação, e ciclos especiais. Esta actividade permanente da Comissão de Engenharia Sanitária visa sobretudo, dentro deste campo específico, fomentar a educação sanitária de base, e a engenharia sanitária, pois estes apresentam-se como sendo os domínios mais carecidios paralelamente com a administra-ção sanitária a nível central e local. A Comissão de Engenharia Sanitária vai levar a cabo dia 16-17 de Julho, um simpósio que versará temas relacionados com as Atribuições e Responsabilidades dos Engenheiros nos Empreendimentos de Saneamento.

OBJECTIVO E PROGRAMA	LOCAL, DATAS, ORGANIZAÇÃO INFORMAÇÕES
4.° Congresso Nacional de Fundição e 3.ª Exposição Nacional de Fundição.	Lisboa (FIL) 26-30 Abril - 72 APF
Quinzena Técnica de Paris Actividades: — Salão Internacional de Material de Obras Públicas e da Construção — Bienal do Equipamento eléctrico e da Automatização dos Processos Industriais — Calafetação, Frio e Climatização	Paris, 25 Maio - 8 Junho - 72 Embaixada Francesa
Expomafer - 72 Problemas de Máquinas - Ferramentas	Porto, 6-14 Maio - 72 Palácio de Cristal

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8.° Congresso sobre irriguação e drenagem	Varna - Bulgária, Maio - 72 48, Nyaya Marg, Chanakyapuri, New Delhi 21 — Índia
Second Cours sur les Methodologies de Planification des Ressources en eau	Trapani, Sicilia,1 - 7 maio - 72 5, Via Valdisavoia, Catania, Italia
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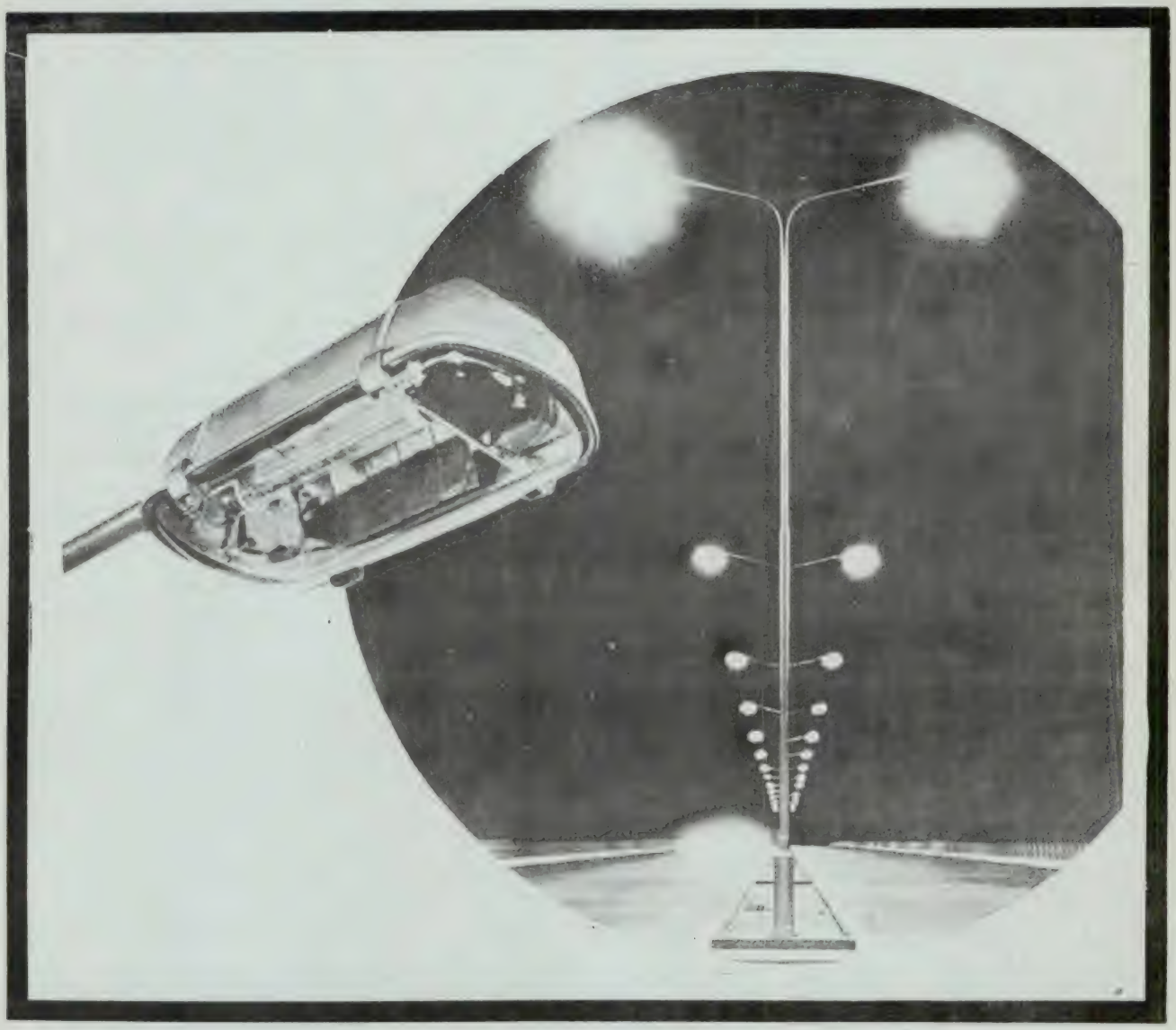

1 Armadura tipo HS, modelos com e sem incorporação dos acessórios, para lâmpada vapor de sódio.

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LIFTING LINE THEORY OF AXIAL FLOW TURBOMACHINES — A REVIEW (*)

A. F. de O. FALCÃO
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SYNOPSIS

The paper presents a review of the literature on the use of lifting line theory in the analysis of the flow through axial turbomachines. The case of screw propellers and open turbomachines, the effects of cylindrical walls, compressibility and rotational flow are successively considered.

RESUMO

Apresenta-se uma revisão bibliográfica sobre a aplicação da teoria da linha sustentadora ao estudo do escoamento em turbomáquinas axiais. São sucessivamente considerados o caso dos hélices propulsores e outros tipos de turbomáquinas abertas e os efeitos devidos à presença de paredes cilíndricas, compressibilidade e rotacionalidade do escoamento.

1. — INTRODUCTION

In the design of axial turbomachines, the analysis of the flow through a blade row is frequently carried out as the combination of two different approaches:

a) Blade element flow, which enables the designer to use the performance data obtained mainly from two-dimensional flow investigations with isolated aerofoils or with linear cascades. It is assumed that the flow about any blade section remains the same regardless of whether the section is in a two-dimensional plane flow field or in an arbitrary annular configuration.

b) Flow induced by the whole blade row or rows. Due to difficulties of the full three-dimensional flow field analysis, simplifying assumptions are always made, leading to different theories. Axial symmetry is one of the most important assumptions, by which the partial derivatives of the flow variables with respect to the angular coordinate are taken equal to zero. Physically, this implies that the blade row is constituted by an infinite number of infinitely thin blades and the shed vorticity (which occurs whenever the circulation around the blade section varies in the spanwise direction) is circumferentially uniform.

There are effects which are not accounted for in the combination of axially symmetric theory and two-dimensional blade element theory. One of these is the fact that the trailing vorticity from the actual blade row is concentrated in the blades' wakes rather than circumferentially uniform. It is expected that this modification to the induced velocity field should be particularly important for relatively small numbers of blades and for considerable variation of the circulation along the span.

2. — LIFTING LINE THEORY

The lifting line theory of axial flow turbomachines follows from Prandtl's theory of wings of finite span [1]**. The blades are replaced by bound vortex lines or lifting lines, which are stationary in the case of linear cascade or stator blades, or are supposed to rotate about a fixed axis in the case of rotor blades, and the velocity circulation at any point of the lifting line is set equal to the circulation about the corresponding blade section.

This simplification is expected to yield good approximations for the resultant forces exerted by the flow upon the blades and to give an approximate picture of the overall flow induced by the blade row,although the flow in the vicinity of a lifting line is definitely different from the flow near a blade surface. In particular, the method can provide a good tool for the study of the interference effects due to the blades and their wakes, but accurate results should not be expected if the blade chord is not small compared with the distance between neighbouring blades.

When the velocity circulation — or the blade load — is not constant along the span, there must be, according to Kelvin's theorem, a wake constituted by free vortex

(*) Received July 1971.

(**) For more recent accounts of Prandtl's theory, see, for example, [2 to 4].

filaments shed by the blade. In the simplified lifting line model, the wakes take the shape of vortex sheets. For isentropic flow, the second vorticity theorem of Helmholz (see e. g. [5]) states that the trailing vortex filaments move with the fluid and, if the flow is steady, coincide with the streamlines.

It follows that the motion of the shed vortex filaments and their instantaneous shapes depend upon the velocity field they induce themselves. The exact treatment of this case leads to a non-linear mathematical problem, the solution of which involves great analytical and numerical difficulties, even for the trivial case of a stationary straight lifting line with a trailing vortex sheet in an undisturbed uniform flow.

In the classical approach to the problem, it is assumed that the trailing vortex filaments have simple geometrical configurations (straight or helical lines), usually coinciding with the primary flow streamlines (or the relative streamlines, in the case of a rotor). This assumption implies that the disturbance — or velocity induced by the bound and trailing vortex systems — is small compared with the undisturbed flow velocity, so that the actual streamlines do not differ considerably from the streamlines of the primary flow. We obtain, in this way, the so called first order flow based on small disturbance linear theory. Prandtl's lifting line theory of wings with finite span is the best known example of this approach.

3. — SCREW PROPELLERS AND OPEN TURBOMACHINES

It is not surprising that the method was first applied to screw propellers, where the circulation, being zero at the blade tip, has a great spanwise gradient and the shed vorticity, concentrated in helical wakes, induces a velocity field about the blades which cannot be neglected without introducing considerable errors. Moreover, as the number of blades is usually small, actuator disc or any other theory based on axial symmetry can only provide a rough approximation to the actual flow.

Three types of approximation are usually considered in propeller vortex theory. In the case of a lightly loaded propeller, the influence of the velocity induced by the bound and trailing vortex systems on the shape of the vortex sheets is neglected. The free vortices are then helices and the vortex sheets constitute true helical surfaces, the pitch of which is determined solely by the ratio of the advance speed to the angular speed. In the case of a moderately loaded propeller, the free vortex lines are still suposed to lie on cylindrical surfaces of revolution but the influence of the tangential and axial components of the induced velocity upon the pitch is now taken into account and the vortex sheets are not, in general, true helical surfaces. Finally, for a heavily loaded propeller, the effect of the centrifugal forces and the contraction of the slipstream are also taken into account.

Betz [6], in 1919, applied, to screw propellers, Prandtl's lifting line theory of wings of finite span and established the condition for minimum energy loss at a given thrust for a moderately loaded propeller: the flow far behind the propeller must be such that the helical surface swept by each blade moves downstream like a rigid body, i. e. the pitch of the trailing vortices does not vary with the distances to the axis of the propeller. By applying certain symmetric properties of the vortex system, Betz showed that the downwash velocity (obtained by combining the tangential and axial componets of the velocity) induced at the spoke lifting lines is one half of the velocity induced at corresponding points of the vortex sheets far downstream. This important relation was later widely used by other research workers and designers. In an appendix to the same paper, Prandtl, replacing the helical vortex sheets by parallel plane sheets, derived an approximate solution for the optimum radial distribution of the circulation.

In 1929, Goldstein [7], using Betz's conclusions, solved Laplace's differential equation for the velocity potential far downstream in a non-orthogonal helical system of coordinates and obtained the radial distribution of the circulation which gives minimum energy loss. In the same paper, numerical results were presented for a two-bladed propeller. More complete evaluations for several numbers of blades were later given by Kramer [8] and, more recently, by Tatchmindji and Milam [9].

Kawada [10, 11], using Goldstein's helical system of coordinates, solved the potential problem far behind a screw propeller with N blades, i. e. for a system constituted by N lifting lines of constant circulation, N free helical vortex lines shed by the blades' tips and an axial straight vortex line of the combined strenght of the lifting lines, extending downstream from the centre of the propeller. The solution involved series in terms of the modified Bessel functions I and K, which, for numerical evaluations, were replaced by Nicholson's asymptotic expressions.

The solution of a similar mathematical problem had been published before by Lamb [12] for the magnetic field of a helix.

Moriya [13], by direct integration of Biot-Savart's equation and also under the assumption of constant blade circulation, obtained the expressions already derived by Kawada for the downwash velocity at points of a lifting line.

Once the velocity field induced by a free helical vortex line of radius ξ is known — this is the problem solved by Kawada — the field, due to a lifting line of variable circulation and its trailing vortex sheet, can be obtained by integration with respect to ξ between $\xi = r_i$ and r_o (respectively the radial coordinates of the blade root and tip). However, a complication arises when the downwash velocity at a point P(r) of the lifting line is to be calculated by this method. In fact, as the radius of the helical line ξ approaches the radial coordinate r of P — i. e. as the starting point of the helical vortex tends to P — the velocity induced at P tends to infinity, which means that the integrand has a singularity at $\xi = r$ and the integral exists only as a Cauchy principal value. This fact obviously makes difficult the application of quadrature methods.

Moriya [14] suggested a method for evaluating the integrals which give the tangential and axial components of the velocity induced at a lifting line of variable circulation, by introducing the so called tangential and axial induction factores. The tangential induction factor is defined by the ratio

$$i_t(r, \xi, \beta) = \frac{v_t(r, \xi, \beta)}{w(r, \xi)},$$

where $v_t(r, \xi, \beta)$ is the tangential component of the velocity induced at point P(r) by a free helical vortex of unit strength, with radius ξ and angle β. In the denominator, $w(r, \xi)$ is the velocity (with tangential direction) induced at P (r) if the helical line is replaced by a semi-infinite straight vortex of unit strength, parallel to the axis of the propeller and extending to infinity from the same starting point. Biot-Savart's law gives

$$w(r, \xi) = \frac{1}{4\pi(\xi - r)}.$$

It is easy to see that $i_t(r, \xi, \beta)$ remains finite, even for $\xi = r$.

The tangential component of the velocity due to the whole vortex sheet is then given by

$$V_t(r) = \frac{1}{4\pi}\int_{r_i}^{r_o} \frac{d\Gamma(\xi)}{d\xi}\,\frac{i_t(r, \xi, \beta)}{\xi - r}\,d\xi,$$

where $\Gamma(\xi)$ is the circulation about the lifting line and β is assumed to be a known function of ξ. The right hand side of the last equation is formally identical to the expression of the downwash velocity of a wing with a span equal to $r_o - r_i$, the equivalent spanwise distribution of the circulation $\Gamma^*(\xi)$ being such tha $d\Gamma^*/d\xi = i_t\, d\Gamma\ d\xi$

A similar analysis applies to the axial component of the induced velocity with the aid of the axial induction factor i_a.

Provided that the induction factors are known, for each value of r, as functions of ξ, the integration can be carried out with the help of methods derived in the theory of wings of finite span. Lerbs [15, 16], extending Glauert's aerofoil method [3], determined the principal value of the integrals by expanding the circulation Γ and the induction factors in Fourier series in terms of a variable related to ξ.

Values of the induction factors were published in the form of diagrams by Moriya, who evaluated, by a graphical method, the integrals arising from the application of Biot-Savart's law, for 2-bladed propellers [14] and later also for 3- and 4-bladed propellers [17]. More detailed and accurate diagrams for 3-bladed propellers were later published by Strscheletzky [18, 19], who obtained the results by direct numerical integration of the Biot-Savart's integrals. Values of the induction factors, for propellers with 3, 4 and 5 blades, were obtained and published in the form of diagrams by Lerbs [15, 16], who used Kawada's analytical solution, with Nicholson's asymptotic expressions replacing the modified Bessel functions I and K. More accurate and extensive numerical results, presented in tables, were later obtained by Morgan [20, 21] with the aid of more approximate asymptotic expressions of the modified Bessel functions.

A different way of dealing with Biot-Savart's integrals was used by Guilloton [22, 23], who wrote the velocity induced at a point r of a lifting line as

$$V(r) = \frac{1}{4\pi}\int_{r_i}^{r_o} \frac{d\Gamma(\xi)}{d\xi}\,\frac{d\xi}{\xi - r} + \frac{1}{4\pi}\int_{r_i}^{r_o} \frac{d\Gamma(\xi)}{d\xi}\,H\,d\xi,$$

where H is a function of r, ξ and the helical pitch, which represents the effect of the helical shape of the trailing vortices (in comparison with the straight vortices assumed in wing theory) and remains finite when $\xi \to r$. Only the first integrand presents a singularity at $\xi = r$ and its integration can be overcome by Glauert's method [3] for wings of finite span. In fact, there still remains, in H, a singularity of the type of $\ln(\xi - r)$, which was found by Guilloton to be practically negligible. Numerical values of the second integral were given by Guilloton in terms of the first two coefficients of the Fourier development of $\Gamma(\xi)$, for several combinations of the geometrical parameters of the propeller.

In all the works refered to, where the concept of induction factor is used, the slipstream contraction and the effects of the centrifugal force are neglected, but the variation of the pitch of the helices with the radius can be taken into account. This means that those methods apply to moderately or to lightly loaded propellers.

A comparison of the results obtained by using some of these lifting line methods in propeller design was presented by Johnsson [24].

A different approach was used by Reissner [25, 26], who solved the potential problem in the far wake of a screw propeller for an arbitrary spanwise distribution of the circulation, assuming that the trailling vortex sheets constitute true helical surfaces. To obtain the appropriate discontinuities of the potential and of the radial component of the velocity across the vortex sheets, he used an artifice which consists in introducing a source distribution of helical symmetry, with a linear saw-tooth circumferential variation, which produces the desired discontinuities. A second source distribution is thereafter superposed, in such a way that its circumferential variation represents a Fourier series of the saw-tooth curve. Poisson's differential equation is solved for both distributions, in a system of helical coordinates identical to that used by Goldstein and Kawada, and, subtracting the second solution from the first one, the flow field induced by a set of equidistantly spaced helical vortex sheets is obtained. Having found the expressions for the downwash velocity induced at the lifting lines (which is equal to one half of the induced velocity at corresponding points of the vortex sheets far downstream, according to Betz's law for semi-infinite helical vortex sheets), Reissner combined these results with blade element two-dimensional theory to establish a relationship between the blade geometry and the induced downwash velocity.

Further developments of the vortex theory of the screw propeller in incompressible flow, including lifting surface theory, can be found in [27 to 30].

4. — THE EFFECT OF CYLINDRICAL WALLS

To evaluate the velocities induced at the blades of a propeller operating in free space, Biot-Savart's equation can be applied without great difficulties and with good results. However, when adjacent boundaries, such as a hub, a duct or both, are present, the condition of zero normal velocity at the walls must be satisfied and the use of Laplace's or Poisson's differential equation for the velocity potential is a more suitable approach, particularly if the walls are cylindrical surfaces. Obviously, in this case, the analytical solutions become more complex.

Takeyama [31] extended Kawada's analytical solution to the case of N symmetrically spaced helical vortices bounded by a circular cylindrical casing extending to infinity in both axial directions. Additional terms to Kawada's expressions were derived by Lerbs [15] to take into account the effects of a cylindrical hub of infinite length.

Hickling [33] presented the expression of the velocity potential for the case of N symmetrically spaced helical vortices enclosed in an annular cylindrical duct of infinite length and also gave the simplified expressions for the cases when only one of the walls is present. The complete solution is given by an infinite series with terms involving cross products of the modified Bessel functions I and K and their first derivatives. With the help of numerical examples, Hickling concluded that the flow field in the midde of the annular duct is only slightly affected by the presence of the walls and that, near the hub or the casing, the solution approaches that of the case when only one boundary is present. With an increase in the number of blades, the effects of the hub and duct walls become confined to smaller regions and, for an infinite number of blades, the boundaries do not affect the flow.

Meyer [34], in 1946, studied the flow in a stationary annular cascade of radial source lines and lifting lines of constant circulation, by integrating Laplace's potential equation in cylindrical polar coordinates by the method of separation of variables. The solutions are expressed by double series involving Bessel functions J and Y of the radial coordinate and circular functions of the angular coordinate. The effect due to the finite number of blades in shown to decay exponentially away from the cascade plane. Meyer also extended, to a stationary annular cascade of blades with constant circulation, Ackeret's [35] singularities method for two-dimensional linear cascades.

The deviation of the two-dimensional approximation (i. e. linear cascade) from the three-dimensional annular cascade of lifting lines of constant strength was studied theoretically by Ginsburg [36], who considered particularly the flow field in the vicinity of the cascade. Using an electrolytic tank, he measured the potential field for a hub/casing diameter ratio of 0,308 and compared the results with the theoretical values.

Rossow [37] extended Ginsburg's theoretical investigation to the region away from the cascade for the cases of radial source lines and radial lifting lines of constant strength. In his analysis, the three-dimensional solution is expanded in a Taylor series about the limiting case of hub/casing diameter ratio equal to one.

The effects of the trailing vorticity in an annular cascade were studied by Nath, who carried out the numerical integration of Biot-Savart's equation for three different cases: straight axial vortex filaments concentrated along symmetrically spaced plane sheets [38]; helical vortex filaments of constant pitch axisymmetrically distributed between coaxial cylinders and shed by an actuator disc [39]; and finally the case of helical vortex sheets equidistantly spaced [40]. The circulation about the lifting lines was taken equal to a third degree polynomial of the radial coordinate, with the first derivative vanishing at the inner and outer walls (in order not to have infinite downwash velocities at the ends of the lifting lines). However, in his three papers, Nath, although considering the problem of ducted fans, neglected the effect of the inner and outer boundaries and, as a consequence, strictly his results (with the exception of the actuator disc) apply only to a propeller or a fan in free space.

5. — COMPRESSIBLE FLOW

In all the works quoted so far, only the case of incompressible flow was considered. The vortex theory of the screw propeller in compressible flow was sketched by Busemann [41]. Davidson [42], using Reissner's analysis [25, 26] for the potential in the far wake, presented a solution for the whole flow field for a propeller of arbitrary circulation in compressible flow. In Davidson's analysis, the propeller is enclosed in a coaxial cylindrical wind tunnel of circular cross section, supposed to extend to infinity in both axial directions. It was later pointed out by Okurounmu [43] that his choice of the boundary conditions at the cascade plane is inappropriate and the solution does not satisfy the continuity requirements for compressible flow.

Following the analysis of McCune [44, 45] for the three-dimensional compressible flow in an annular cascade of source lines, Okurounmu and that author [43, 46] studied the case of a rotating annular cascade of lifting lines of prescribed variable circulation in compressible flow. Using a non-orthogonal helical system of coordinates, as Goldstein, Kawada and Reissner had done for the screw propeller, they showed that, far downstream from the rotor, the velocity field can be expressed in terms of only two coordinates — the radius and the helical angular coordinate — not explicitly dependent on the axial coordinate, and the solution has the same form as for the case of incompressible flow. The expressions for the potential far downstream were obtained by extending Reissner's results to take into account the presence of cylindrical walls, and the

expressions for the complete flow field were then obtained by superposing, on the far wake solution, a true three-dimensional solution that decays exponentially to zero with the distance to the cascade plane and which includes the compressibility effects.

6. — ROTATIONAL FLOW

In all the works refered to before, either those using Biot-Savart's law or based on the velocity potential, it is explicitely or implicitely assumed that the disturbance flow field is irrotational everywhere except at the singularities (the bound and trailing vortex lines). As we show below, this assumption implies that the primary or undisturbed flow — i. e. the flow in the absence of blades — is irrotational. However, in many problems of fluid mechanics in turbomachines, the actual flow field differs considerably from the conditions of irrotationality, due to the presence of wall boundary layers or to the passage through stationary or rotating rows of blades.

If the primary flow is not irrotational everywhere, the effect of the disturbance due to the blades is to alter the pattern of the streamlines and, consequently, also the pattern of the primary flow vortex lines convected by the flow.

If the velocity disturbance is of order (ε) (the primary flow velocity V_0 being of order of unity and ε being a small quantity), the disturbance to the vorticity vector field is of order of $\varepsilon\Omega_0$ (where $\vec{\Omega}_0 = \text{curl}\,\vec{V}_0$ is the vorticity vector in the primary flow). It follows that, unless it is $\Omega_0 = 0$ everywhere, the disturbance flow outside the bound and trailing vortex systems is rotational, with vorticity of order of $\varepsilon\Omega_0$.

If the primary flow vorticity Ω_0 is everywhere small, say $O(\varepsilon)$, we have $\varepsilon\Omega_0 = O(\varepsilon^2)$ and, neglecting quantities of $O(\varepsilon^2)$ or smaller, we can take the disturbance as irrotational. This is the first approximation in Hawthorne's theory of shear flow [47, 48] — small shear, small disturbance.

If, however, Ω_0 is $O(1)$, the vorticity of the disturbance flow is $O(\varepsilon)$, i.e., is of the order of the velocity disturbance itself and cannot be neglected(*). The secondary flow field must, therefore, be considered as rotational. This case corresponds to Hawthorne's second approximation — large shear, small disturbance.

Some solutions concerning small perturbation due to lifting systems in parallel shear flow can be found in the literature. One of the earliest contributions is the work by von Kármán and Tsien [49], who extended Prandtl's lifting line theory to the more general case of a rotational primary flow. Honda [50], using a lifting surface theory, obtained a solution for the case of incompressible shear flow about a thin wing spanning two parallel walls and later [51] extended the solution to the case of a linear cascade of thin blades in incompressible shear flow. Numerical results for this last problem were obtained by Nally and Hawthorne [52] with the aid of a digital computer. Namba and Asanuma [53, 54] studied the case of a rectilinear cascade of lifting lines in subsonic shear flow and later Namba [55] extended Honda's incompressible flow analysis to the case of a linear cascade of thin blades in subsonic shear flow. A more general and detailed analysis of shear flow problems can be found in a work by Hawthorne [47].

(*)The vorticity being given by a first order differential operator of the velocity, it follows that a vorticity field of $O(\alpha)$ will induce a velocity field of the same order of magnitude if the representative spatial dimensions of the field (e.g., the cascade pitch) are $O(1)$.

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FEIRAS, CONFERÊNCIAS, EXPOSIÇÕES E CURSOS NO MUNDO

OBJECTIVO E PROGRAMA	LOCAL, DATAS, ORGANIZAÇÃO INFORMAÇÕES
Europress Engineering 72	15 - 17 de Maio - 72 Genoa, Itália Istituto Internazionale delle Comunicazioni Villa Piaggio, Via Pertinace 16125 Genoa, Italy
Organização da Gestão e Conservação das Instalações Industriais	Lisboa, 15 - 19 Maio - 72 COPRAI
Congresso sobre Modelos Estruturais	Sydney, 16 - 18 Maio - 72 Prof. H. J. Cowan; Dept. of Architéctural Science, un. of Sydney, Sydney 2006, Austrália
Spring Joint Computer Conference	Atlantic City, 16 - 18 Maio - 72 P. O. Box 401, Montvale, New Jersey 07645, U. S. A.
National Petroleum Show	Calgary, Alberta, Canada, 16 - 19 Maio - 72 P. O. Box 1010, Postal Station B, Toronto 2 B Canada
XXV° Journées CEBEDEAU: eau, air corrosion	Liège, 16 - 19 Maio - 72 2, R. A., — Stevart, 4000, Liège, Belgica

OBJECTIVO E PROGRAMA	LOCAL, DATAS, ORGANIZAÇÃO INFORMAÇÕES
5.° Congresso Internacional sobre Corrosão Metálica	Tokio, 21 - 27 Maio - 72 National Reg. Inst. Formetals, 2 - 3 - 12 Nakameguro, Meguro - Ku, Tokio, Japão
Symposium on Problems of Water Resources Systems Tema: General Problems/Methods of Design and Control/Economic Problems	Carlsbad, Checoslováquia, 23 - 25 Maio - 72 Dúm Techniky Cvts Praha, Ing. Jarmila Milosova, Gorkého Nám 23, Praga 1 Checoslováquia.
Coordination entre la Foresterie et les Industries ou Bois	Helsinquia, 23 - 31 Maio - 72 ONU
Salon International du Matériel de Travaux Publics et de Bâtiment — Expomat	Le Bourget, 25 Maio - 4 Junho - 72 Embaixada Francesa
Drupa - 72 Feira de Máquinas de Impressão, Transformação de papel e Artigos Gráficos	Düsseldorf, 26 Maio - 8 Junho - 72 Câmara de Comércio Luso - Alemã
Congrès: L'Hydrogène dans les Métaux	Paris, 29 Maio - 2 Junho - 72 92 - Chatenay - Malabry - França
2.° Simpósio Internacional sobre energia de origem rádio-isotópica	Madrid, 29 - 5 a 2 - 6 Junta de Energia Nuclear (Espanha)
7th Congress of the International Anti-Noise Association	Dresden, 29 - 5 a 2 - 6 Secretariat of Kamuner der Technik 108 Berlin, Clara - Zetkin - Str., 115 - 117 German Democratic Rep DDR
Comportement des chaussées rigides et aplication à leur dimensionnement	Paris, 30 Maio - 72 ITBTP
Canadian Computer Show	Montreal, 30 Maio - 1 Junho - 72 481 Un. Av. Toronto 2, Canada
VI Bienal do Equipamento Eléctrico e da Automatização dos Processos Industriais	Paris, 31 Maio - 8 Junho - 72 Av. De la Division Leclerc, Puteaux Paris França
Salon International Radio-Télévision - Electroacoutique	Paris, 31 Maio - 12 Junho - 72
Curso de métodos numéricos e experimentais em transmissão de calor e massa	Lisboa, 1 - 5 Maio - 72 Núcleo de Estudos de Engenharia Mecânica (I. A. C.) — I. S. T.

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SISTEMA PARA MEDIÇÃO DE TEMPOS CURTOS DE PROPAGAÇÃO DE ONDAS SÍSMICAS

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RESUMO

Trata-se dum sistema para medição do tempo de percurso duma frente de onda entre dois pontos afastados de 1 a 5 metros, visando a caracterização dum maciço rochoso do ponto de vista de resistência mecânica. Referem-se em especial as unidades electrónicas desenvolvidas no LNEC e comparam-se as suas características com as do equipamento corrente de prospecção sísmica.

SYNOPSIS

This work concerns a system for measuring the travel time of a wave front between two points distant from 1 to 5 meters with a view to characterizing a rock mass from the viewpoint of mechanical strength. The LNEC's electronic units are described in more detail and their characteristics are compared with those of the current equipment for seismic exploration.

1 — INTRODUÇÃO

A caracterização de formações geológicas do ponto de vista de resistência mecânica pode efectuar-se a partir das respectivas velocidades de propagação obtidas em ensaios sísmicos. A exploração desta potencialidade tem especial interesse quando efectuada em conjunto com ensaios estáticos, tendo em vista o estudo comparativo dos resultados.

Para que os dois métodos sejam correctamente correlacionáveis torna-se porém necessário adoptar um dispositivo sísmico de dimensões suficientemente pequenas para que seja respeitado o carácter local do ensaio. Desta circunstância resulta um método de medida, parcialmente diferenciado em relação ao da prospecção sísmica clássica, a que se dá a designação de microssísmico e para o qual foi desenvolvido o equipamento que se apresenta nesta memória.

2 — TÉCNICA DE MEDIDA DO MÉTODO MICROSSÍSMICO

Na figura 1, apresenta-se o esquema de medida do método microssísmico. A actuação do explosor faz detonar uma cápsula, originando uma onda sísmica que é captada sucessivamente por dois geofones. Os respectivos sinais eléctricos, depois de amplificados, são exi-

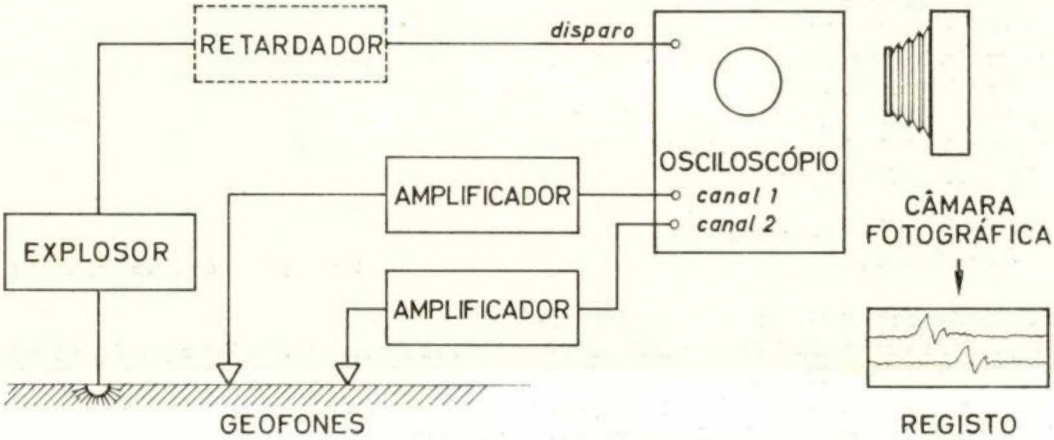

Fig. 1 — Esquema de medida do método microssísmico

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bidos nos dois canais do osciloscópio, cuja base de tempo é disparada, com ou sem atraso, a partir dum impulso fornecido pelo explosor. Há apenas uma passagem do feixe que é fixada fotogràficamente de modo a permitir avaliar o tempo de percurso da frente de onda entre os dois pontos de captação.

Explosor e geofones são aparelhos que fazem parte do equipamento corrente de prospecção sísmica.

Em relação a este a principal diferença reside na unidade de registo. A necessidade da sua substituição pelo sistema osciloscópio câmara fotográfica resulta de serem bastante mais curtos os intervalos de tempo a medir. Com efeito, a distância entre geofones poderá variar entre 1 e 5 metros, a que, para uma velocidade de, por exemplo, 2000 metros por segundo, correspondem tempos de percurso entre 0,5 e 2,5 milissegundos. Para se medir com suficiente resolução dentro desta gama é necessário um sistema de registo com uma base de tempo bastante mais rápida do que podem proporcionar os aparelhos de prospecção sísmica.

Quanto aos amplificadores e retardador de impulsos, dado que se construíram unidades especialmente destinadas ao método microssísmico, serão objecto dum tratamento mais pormenorizado.

3 — AMPLIFICADORES SÍSMICOS

3.1 — *Sobre as características do sinal microssísmico*

No método microssísmico poderiam, em princípio, utilizar-se amplificadores sísmicos clássicos. Esta solução não é contudo a mais conveniente, pois existem certas diferenças quanto às caracteristicas mais apropriadas para cada um dos tipos de ensaio.

No que respeita a ganho, as necessidades do método microssísmico são bastante inferiores aos máximos disponíveis nos amplificadores de prospecção. Este facto resulta das menores dimensões do dispositivo, pois, em regra, a distância do ponto de tiro ao geofone mais afastado não ultrapassará a dezena de metros.

Quanto à resposta em frequência, um amplificador de prospecção está limitado inferior e superiormente a valores da ordem de 10 ciclos por segundo e 300 ciclos por segundo, banda que não é a mais conveniente para o método microssísmico.

De facto, o espectro de amplitude dum impulso sísmico captado à distância $\underline{x}$ do ponto de explosão pode considerar-se da forma [1]:

$$A_x(\omega) = A_0(\omega)\, \varepsilon^{-\alpha(\omega)\, x}$$

em que a constante de amortecimento $\alpha(\omega)$ é crescente com ω e dependente das características do meio, dimido com o seu grau de consolidação.

Atendendo a que a prospecção sísmica se aplica em geral em meios heterogéneos, incluindo com frequência um solo, e que o método microssísmico tem em vista o ensaio de maciços rochosos, a constante α será em regra mais pequena neste caso. Como, por outro lado, as distâncias são também menores, o mesmo amortecimento ocorre no segundo caso a uma frequência mais alta do que no primeiro.

Conclui-se portanto que o espectro do impulso típico de método microssísmico ocupa uma banda de largura superior à do sísmico.

3.2 — *Características dos amplificadores*

A anterior conclusão foi confirmada por experiências que permitiram especificar, para projecto dos amplificadores, uma largura de banda compatível com uma boa relação sinal - ruído. Também por via experimental, foi estabelecido um valor conveniente para o ganho.

O dimensionamento foi ainda condicionado a um baixo factor de ruído, baixa impedância de saída, consumo reduzido e uma impedância de entrada relativamente baixa, adequada às características dos geofones. O circuito inclui um atenuador de entrada, dois andares amplificadores e um andar de colector comum.

As características dos amplificadores (unidade AS-03, frequência de ensaio 500 c/s) são as seguintes:

Ganho: máximo 530, em escalões nominais de 500, 200, 100, 50, 20 e 10.
Largura de banda: — 3 db a 59 c/s e 6,6 kc/s
Impedância de entrada: 950 Ω
Impedância de saída: 140 Ω
Amplitude máxima de saída: 5V, pico a pico
Tensão de ruído equivalente à entrada (gerador - - 220 Ω, ganho — 500): 1 μV, valor eficaz
Tensão de alimentação: 9 V
Consumo: 2 mA

Os amplificadores foram construídos com a forma cilíndrica (figuras 2 e 3) que é apropriada a uma aplicação com muito interesse do método microssísmico: o ensaio de maciços em profundidade, ao longo de furos de sondagem. Esta forma permite a introdução dos aparelhos nos furos de modo a encurtar, com vantagem do ponto de vista de ruído, os cabos de ligação aos geofones.

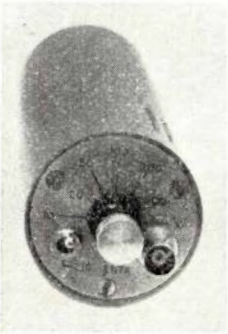

Fig. 2 — Aspecto exterior do amplificador

Foi também projectada uma blindagem estanque (figura 4) que protegerá os amplificadores nos casos, bastante frequentes, em que os furos contenham água.